Reinhold Environmental Ltd.

2010 NOx-Combustion Round Table & Expo Presentation

February 8 & 9, 2010   Chattanooga, TN

CORMETECH

Reinhold Environmental NOx Roundtable

SCR 101 Workshop
Cormetech, Inc.

February 8, 2010

CORMETECH

CORMETECH

Jeremy Freeman

Manager, Engineering Services

freemanjt@cormetech.com

(919) 595-8714

Agenda

CORMETECH

- SCR Reaction Chemistry
- SCR Catalyst Physical Arrangement
- Equipment and Installation Photos
- SCR System Design Considerations
- Catalyst Deactivation Mechanisms
- SCR Performance Monitoring

SCR Reaction Chemistry

CORMETECH

SCR Reactions

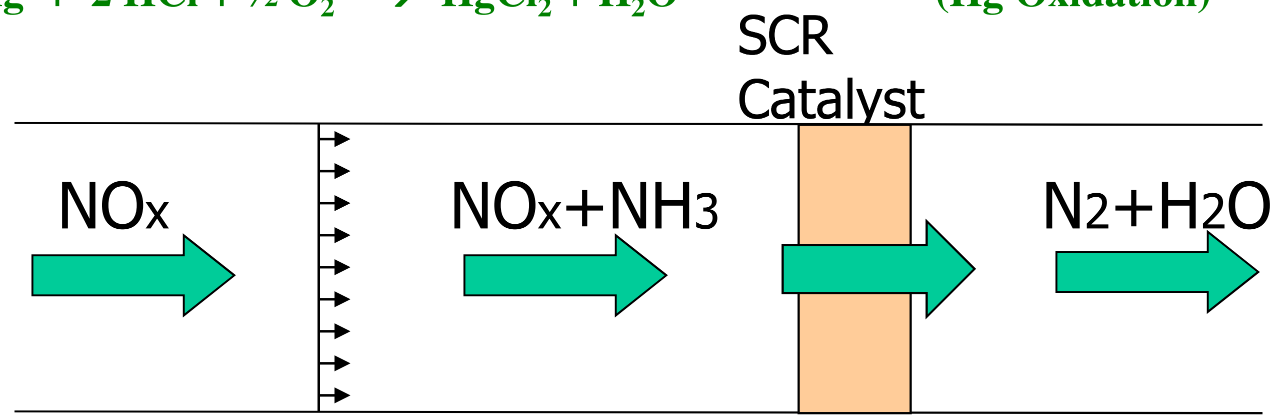
Desired Reactions:

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ (NO$_x$ Reduction)

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ (NO$_x$ Reduction)

$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ (NO$_x$ Reduction)

$Hg + 2\,HCl + \frac{1}{2}O_2 \rightarrow HgCl_2 + H_2O$ (Hg Oxidation)



Undesired Reactions:

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ (SO$_2$ Oxidation)

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (Ammonia Oxidation)

$NH_3 + SO_3 + H_2O \rightarrow NH_4SO_4$ (Ammonia BiSulfate)

$HgCl_2 + NH_3 + \frac{1}{4}O_2 \rightarrow Hg + 2\,HCl + \frac{1}{2}N_2 + \frac{1}{2}H_2O$ (HgCl$_2$ Reduction by NH$_3$)

$HgCl_2 + SO_2 + H_2O \rightarrow Hg + 2\,HCl + SO_3$ (HgCl$_2$ Reduction by SO$_2$)

Reaction Mechanism Description

CORMETECH

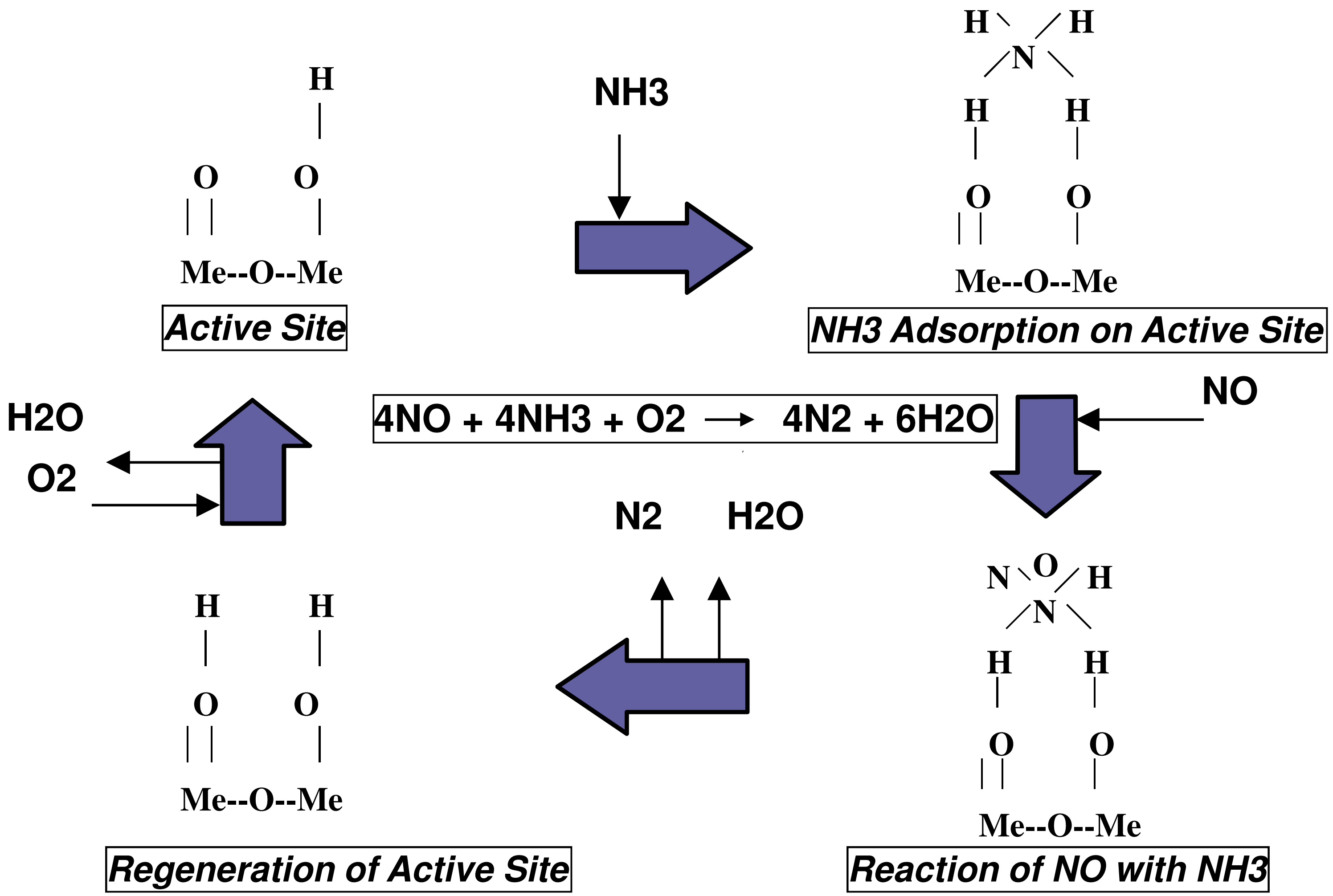
- The NO–NH_3 reaction occurs on the catalyst surface via the mechanism shown on the following slide:
  - Mechanism is a Redox reaction of the Redeal-Eley type

1. NH_3 (absorbed on active sites) and NO (in flue gas) combine into active complex compound, N_2 and H_2O are generated, and metals on active sites are reduced
2. The reduced metals are oxidized by O_2, and active sites are regenerated

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$$

Reaction Mechanism Description

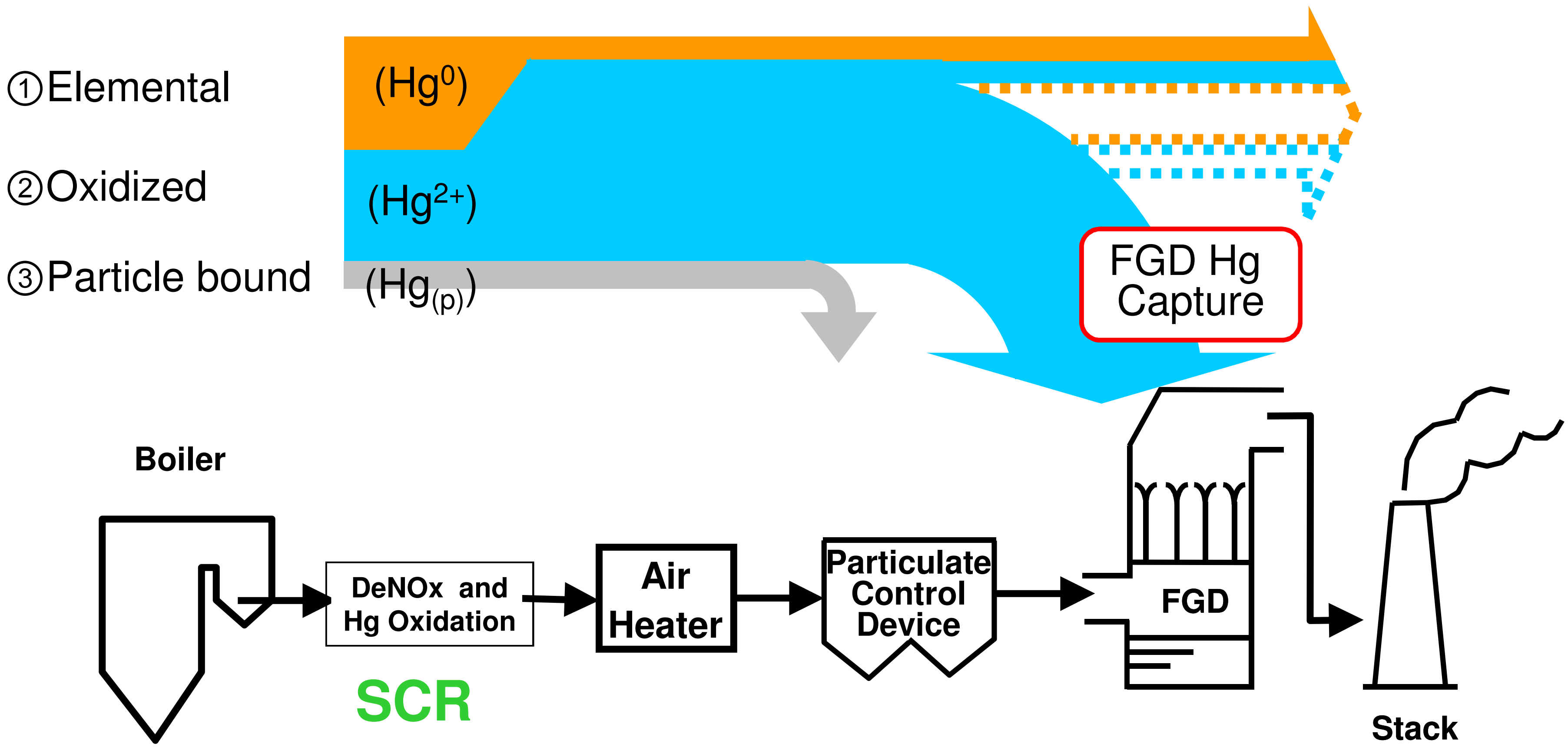
CORMETECH



SCR Co-Benefit for Mercury Capture

CORMETECH

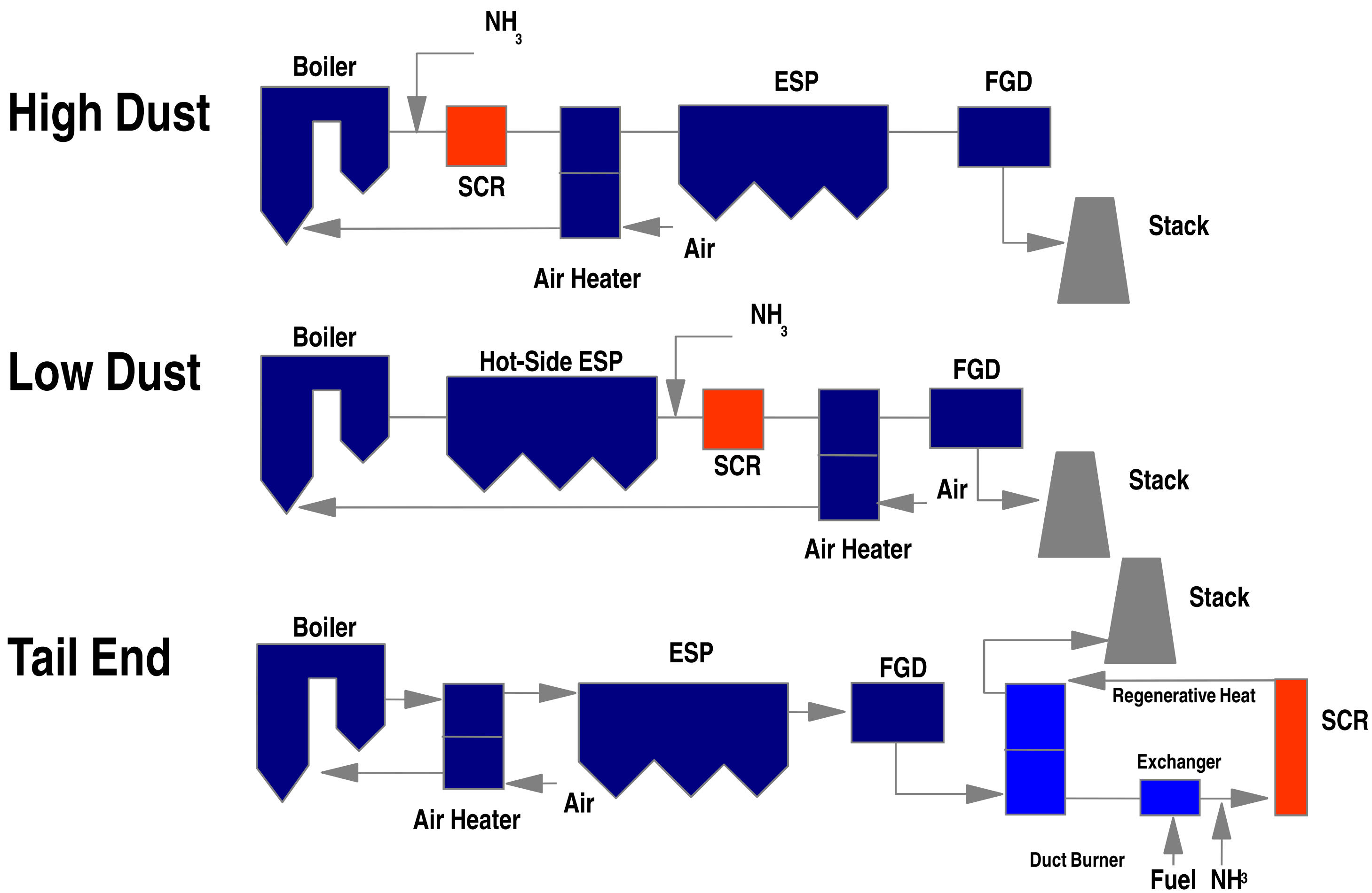
$Hg + 2\,HCl + \frac{1}{2}\,O_2 \rightarrow HgCl_2 + H_2O$ (Hg Oxidation)



CORMETECH

Physical Arrangements

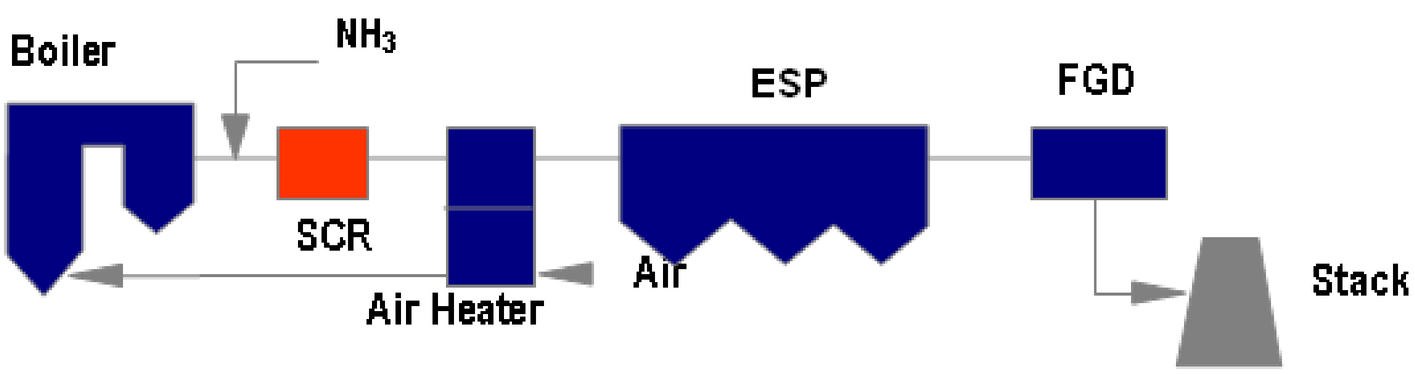
SCR Configurations



SCR Arrangement – High Dust

CORMETECH

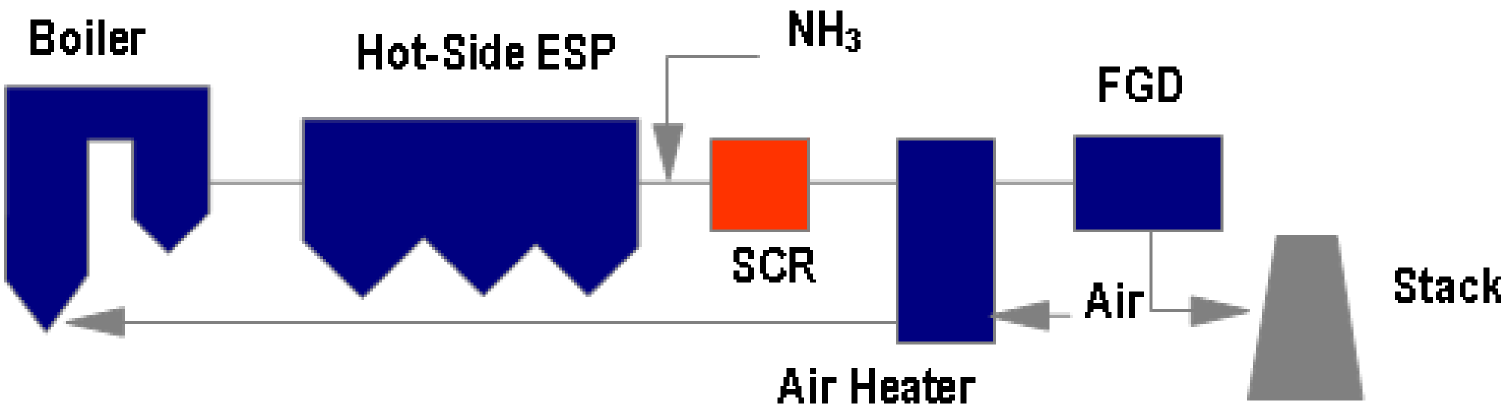
- In the case of a coal-fired boiler, the SCR system can be located in three different arrangements. Temperature is critical to SCR performance. The ideal temperature for SCR is typically 350–400°C at full load. As a result, the most common location for the SCR catalyst is between the economizer and air preheater. Because this location is upstream of any particulate removal system, having the SCR catalyst there is known as a high dust arrangement.



SCR Arrangement – Low Dust

CORMETECH

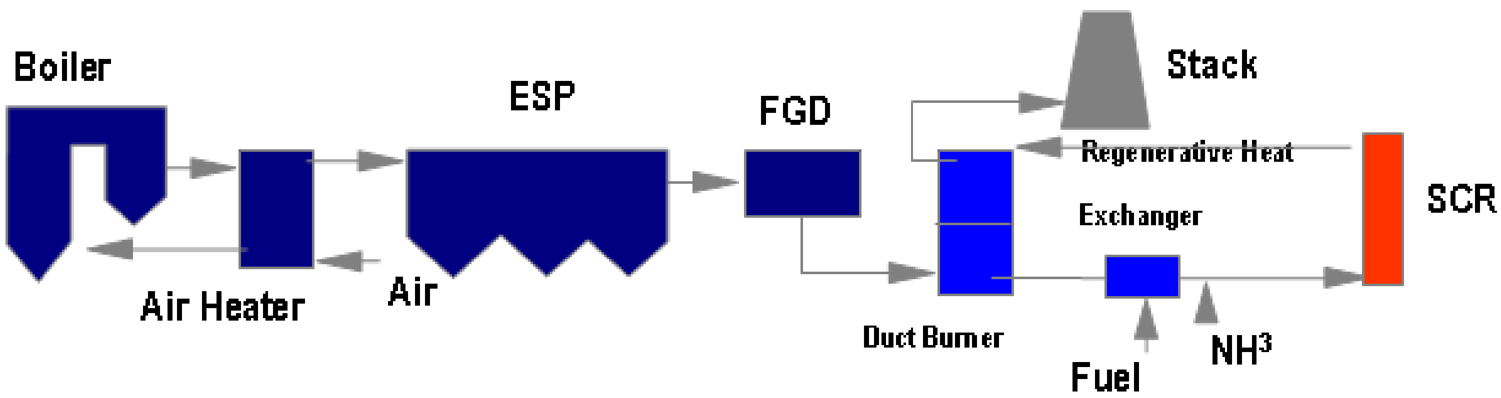
- A less common approach is to locate the SCR downstream of a hot-side electrostatic precipitator (ESP) and upstream of the air pre-heater. This arrangement is known as low dust. The poor performance of hot-side ESP and the fact that the SCR catalyst can withstand high dust loads have made this arrangement less popular over time.



SCR Arrangement – Tail End

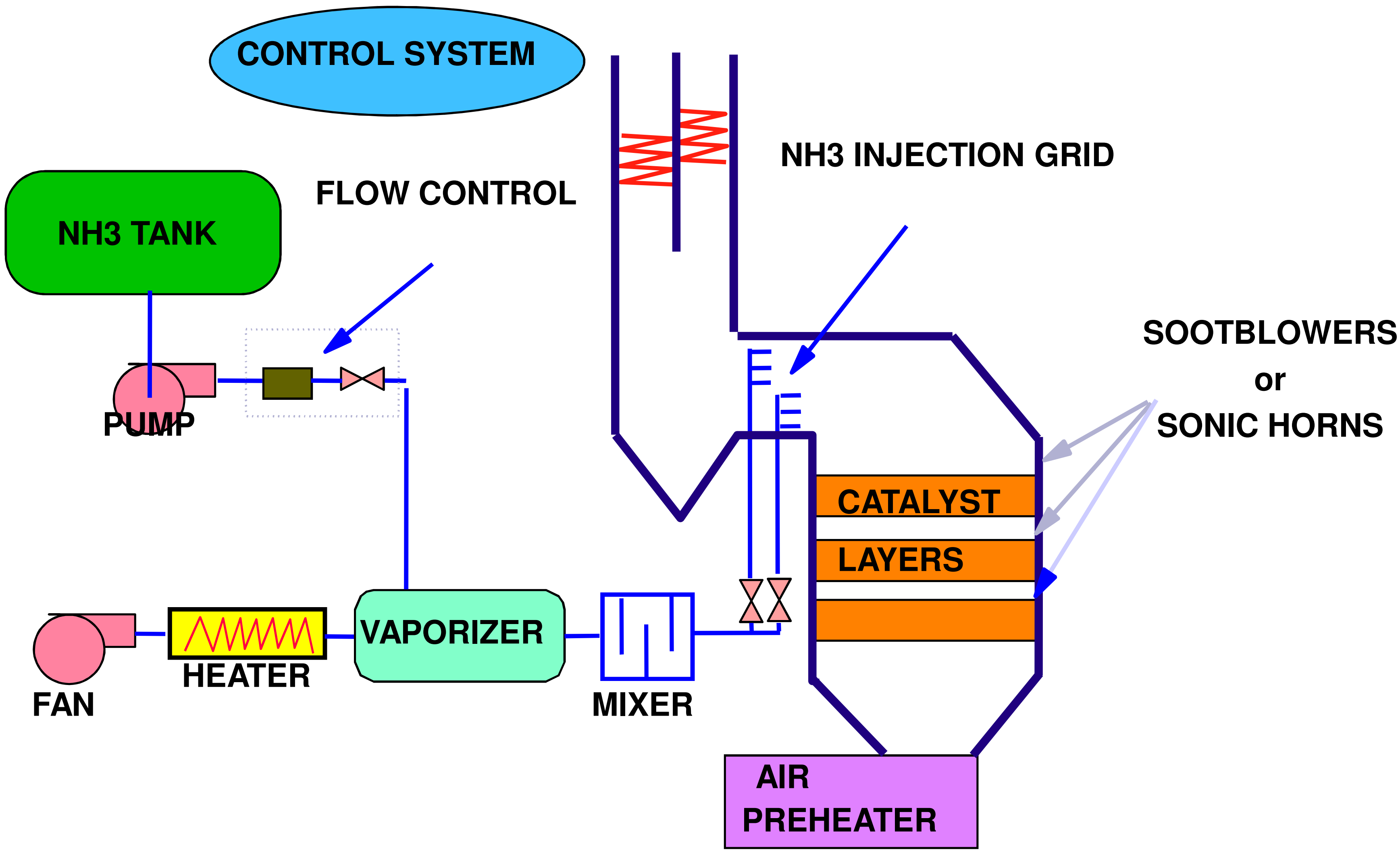
CORMETECH

- The final and least common arrangement is the tail-end SCR system. In this case, the SCR is placed downstream from the FGD equipment. While this has the advantage of providing a flue gas stream which is virtually free of dust and catalyst poisons, the fact that the flue gas must be reheated usually makes this arrangement economically unattractive.



SCR Components

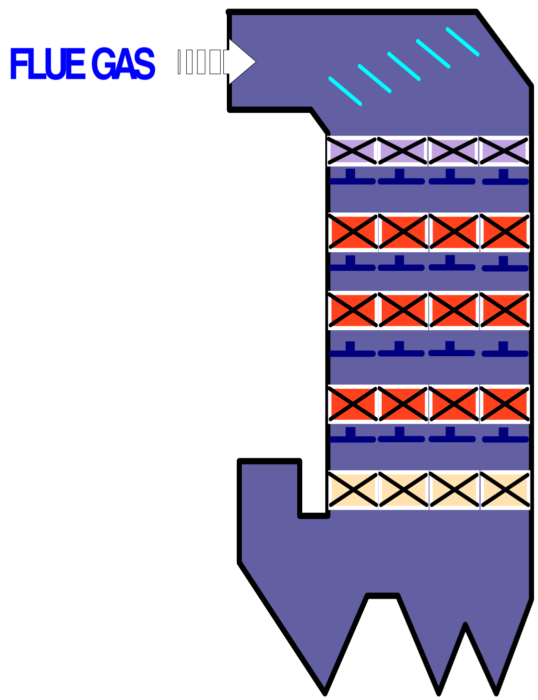
CORMETECH



SCR Reactor Layout

CORMETECH

- Max & min velocity requirements
  - Function of load swing
  - Dust loading
  - Orientation
- Reactor flow modeling
  - Flue design
  - Transitions
  - Bypass
    - SCR
    - Economizer
    - Damper selection



- Accessibility
  - Number of catalyst layers
  - Catalyst loading method
  - Sootblower /Sonic Horn arrangement
  - Measurement ports
- Support Method
  - Hanging or base supported
- Insulation requirements

Catalyst Layer Arrangement

CORMETECH

- Layer arrangement for SCR reactors:
  - Two initial layers plus one future layer (2+1)
    - Most common
  - Three initial layers plus one future layer (3+1)
    - Somewhat common
  - Two initial layers plus two future layers (2+2)
    - Somewhat common
  - Two layer designs (1+1 or 2+0)
    - Rarely utilized

CORMETECH

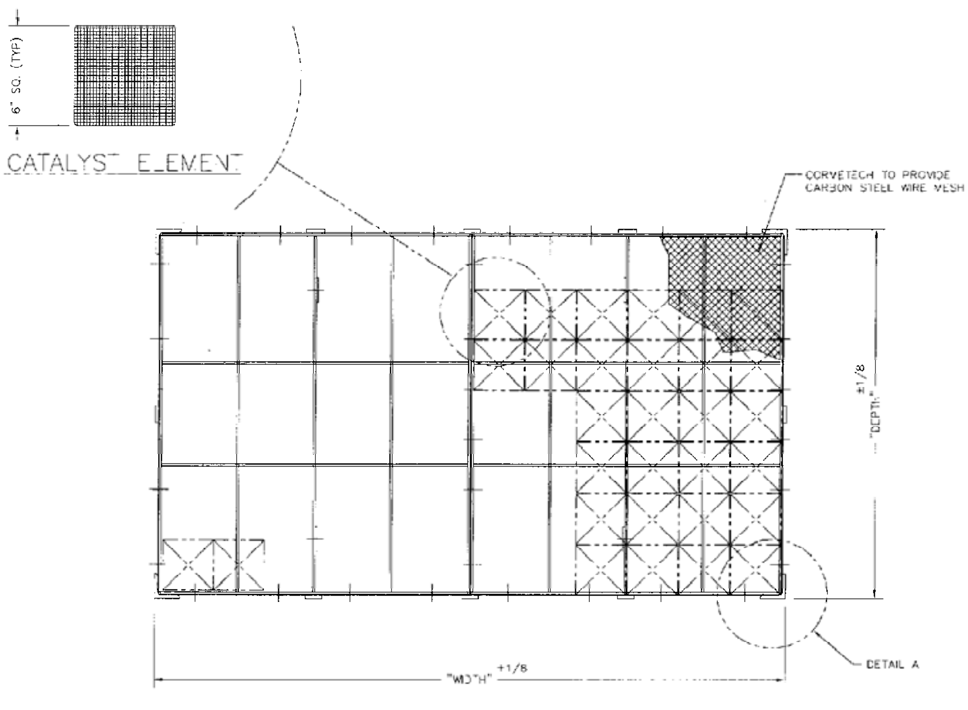
Equipment and Installation Photos

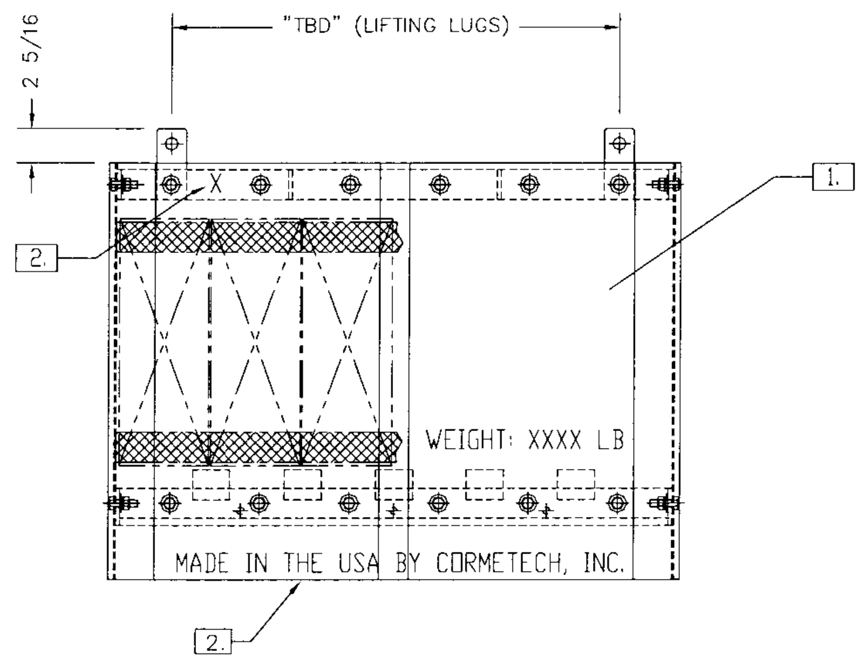
CORMETECH

Catalyst Module Configurations

- Coal SCR Module 'Universal Design'

  Cross section ~ 1 x 2 m





Catalyst Installation

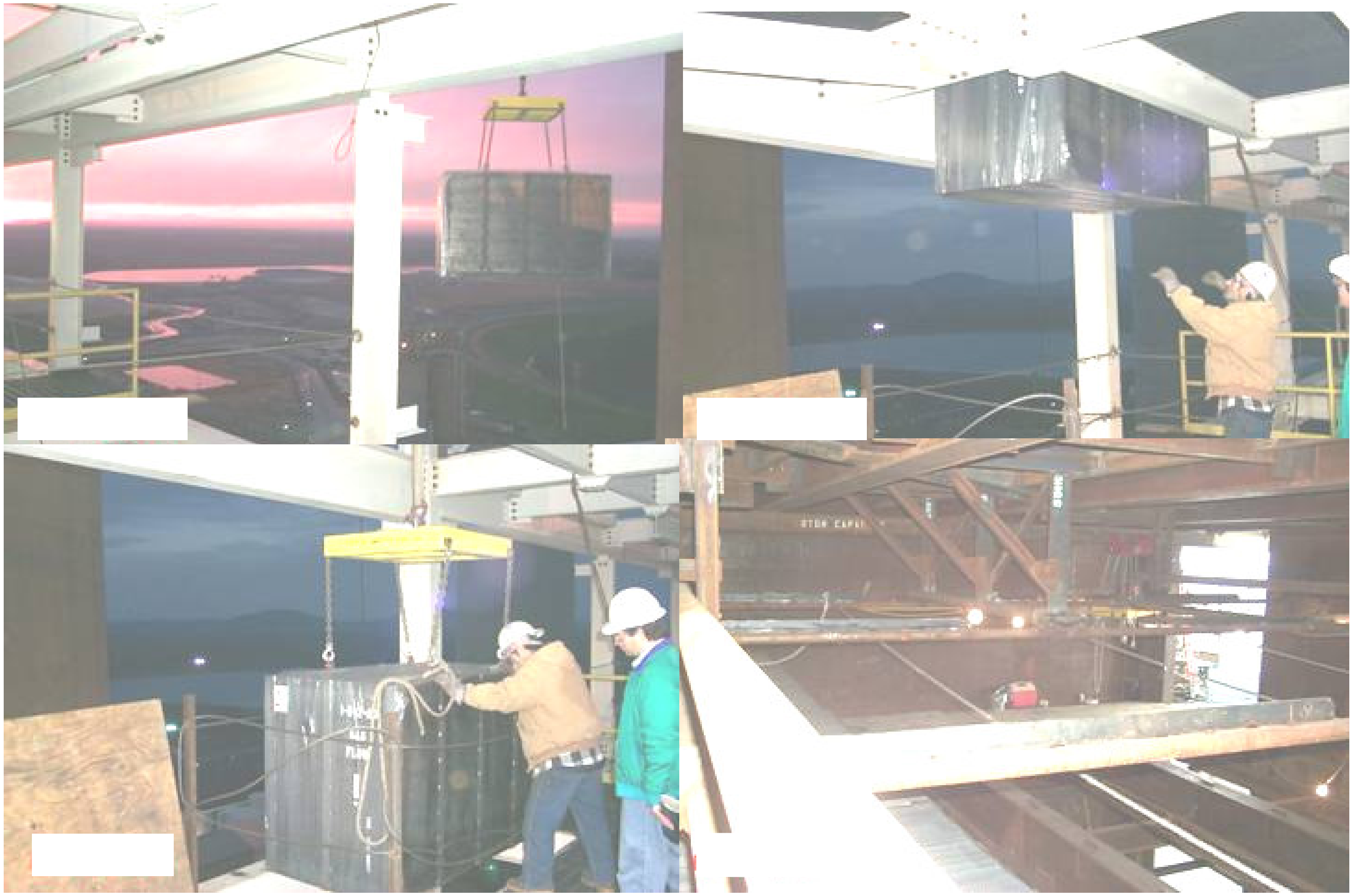
Module Preparation

Catalyst Installation

Roller Conveyor & Tie-off

CORMETECH

Catalyst Installation
Hoist



Catalyst Installation

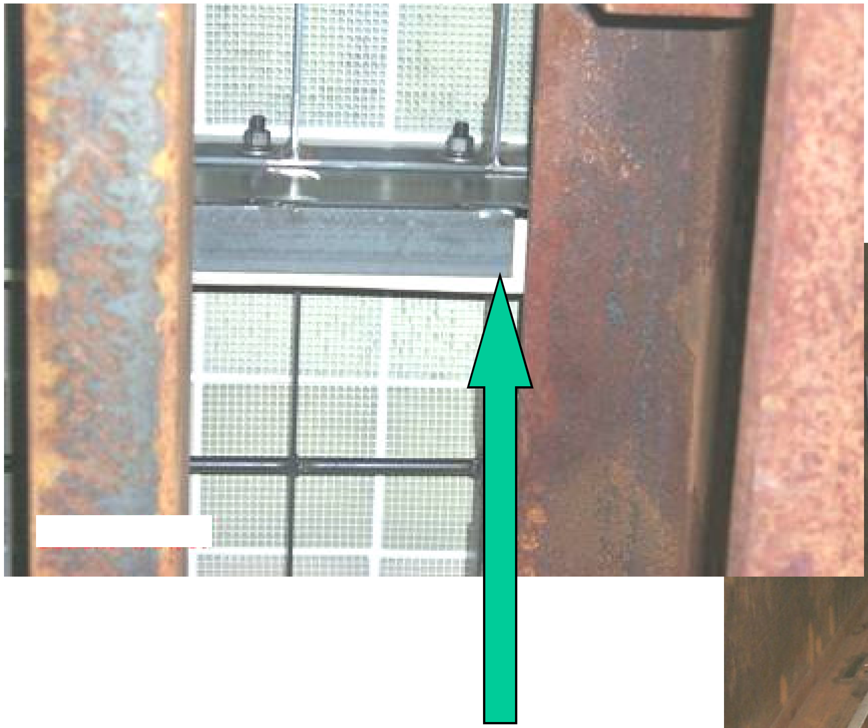
Internal - Carts

CORMETECH

Catalyst Installation
Dust Shields

CORMETECH

Catalyst Installation
Seals



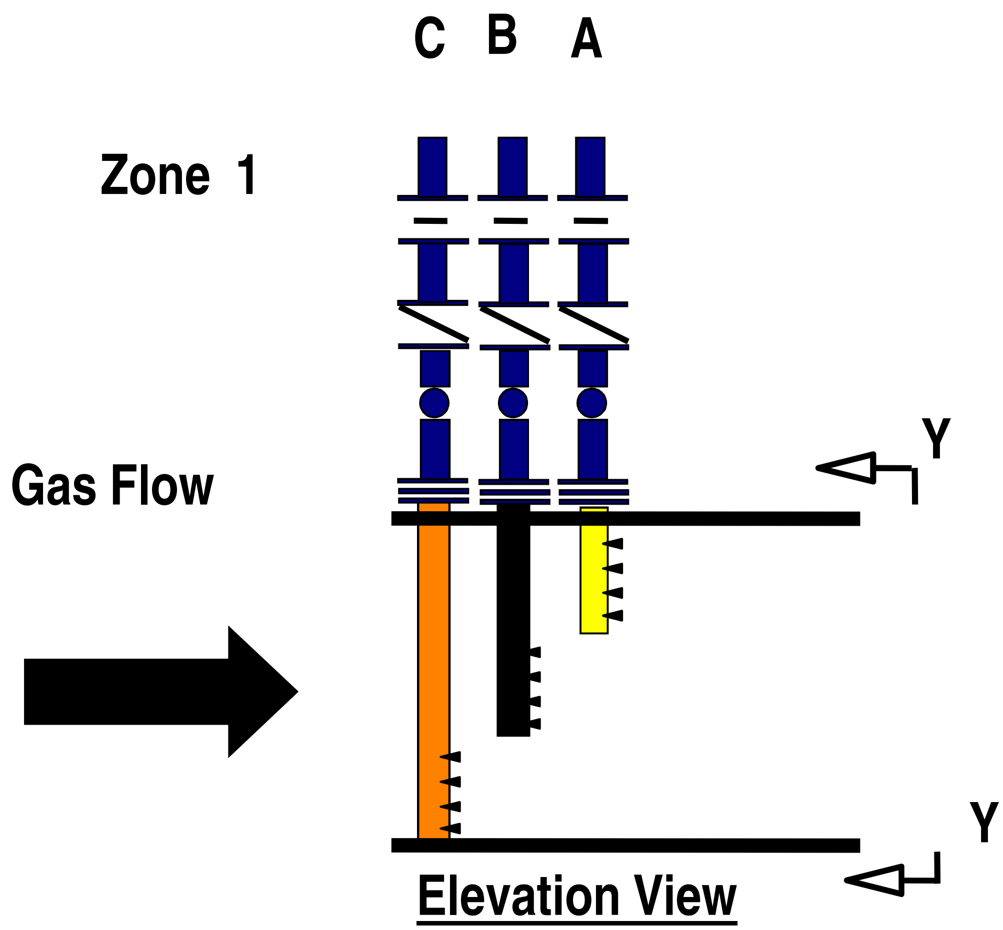
Ammonia Injection Grid

CORMETECH

- Ammonia injection grid (AIG) types
  - Adjustable
  - Fixed
    - Limited adjustment
- Static mixers - mixing control
  - Ammonia mixing
  - Temperature mixing
  - Local or gross mixing, depending upon need/ interface with AIG
- AIG tuning
  - Permanent measurement grid

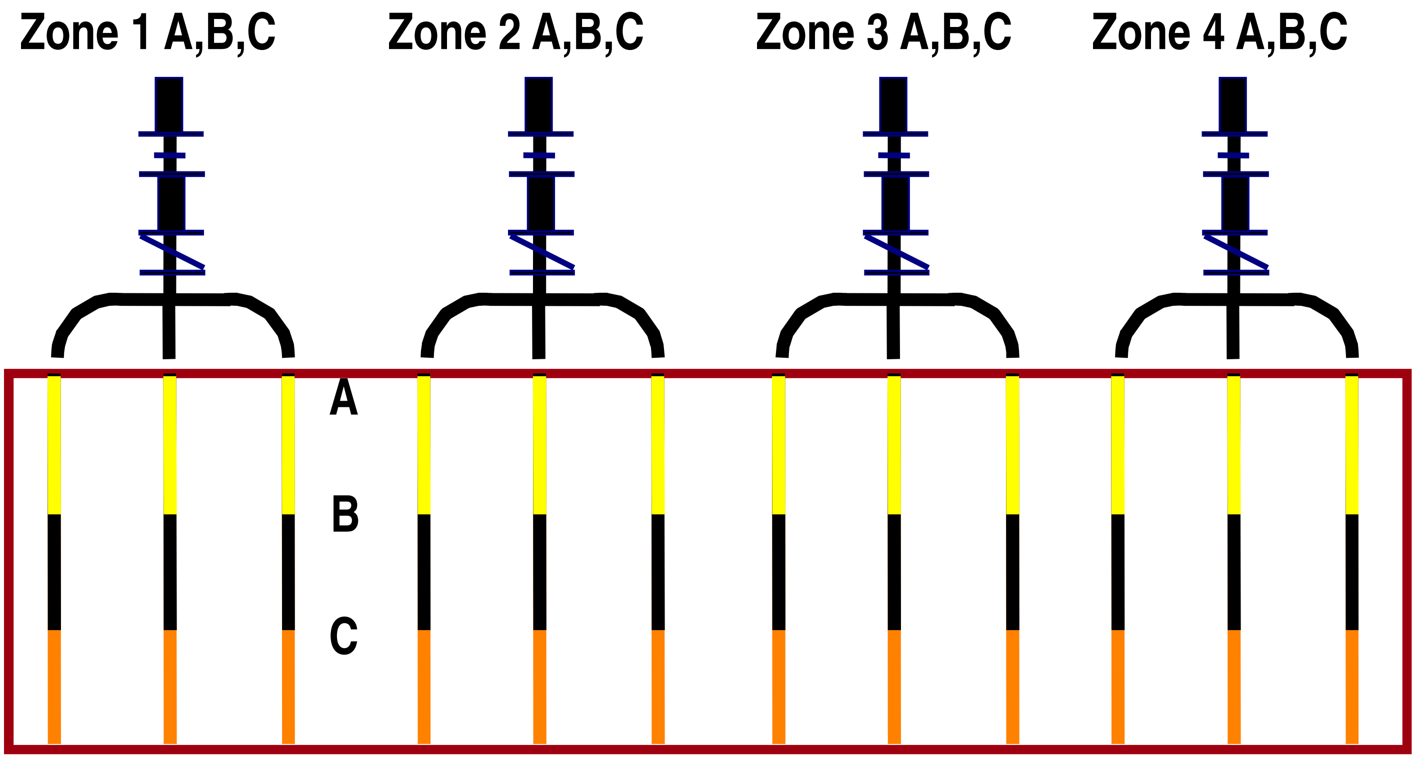
Adjustable AIG

CORMETECH



Adjustable AIG

CORMETECH



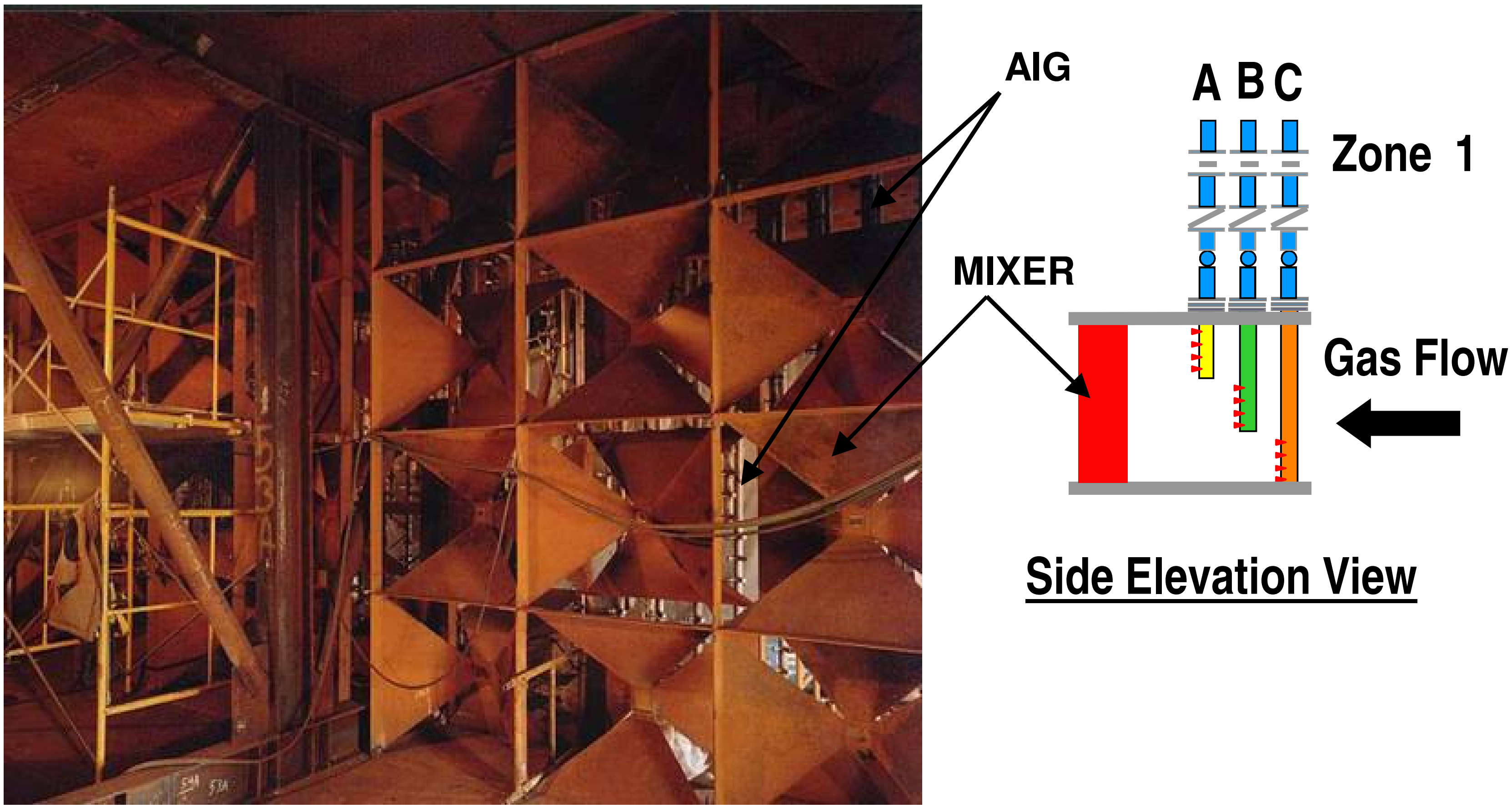
Section Y-Y

AIG Tuning Header

CORMETECH

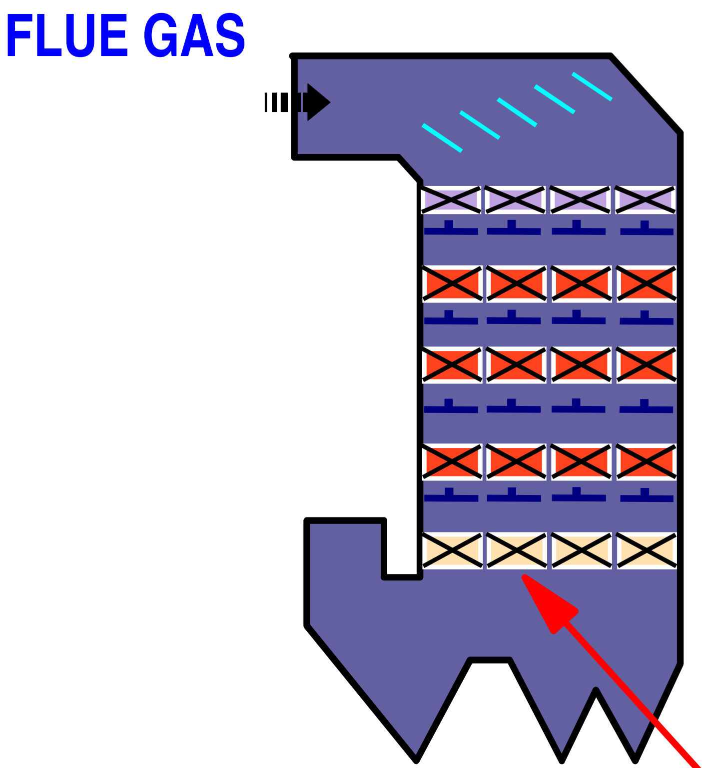
AIG and Mixer

CORMETECH



AIG Tuning

CORMETECH



- Permanent measurement grid utilized below last layer of catalyst.
- Grid used to measure NOx distribution.
- NOx distribution used to adjust AIG to avoid high slip areas.
- Localized slip measurements taken at low NOx areas to assure max slip is below acceptable level.

Measurement Grid

(Layout dependent on reactor size)

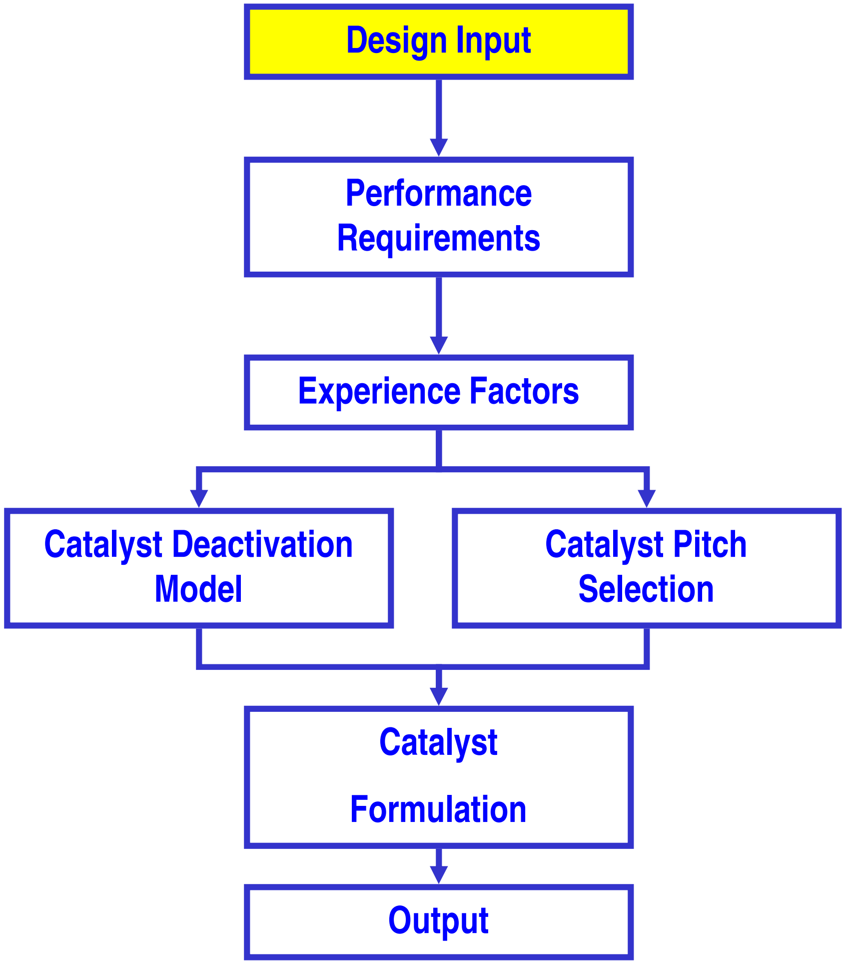
CORMETECH

SCR System Design Considerations

CORMETECH

Catalyst Design Process

CORMETECH

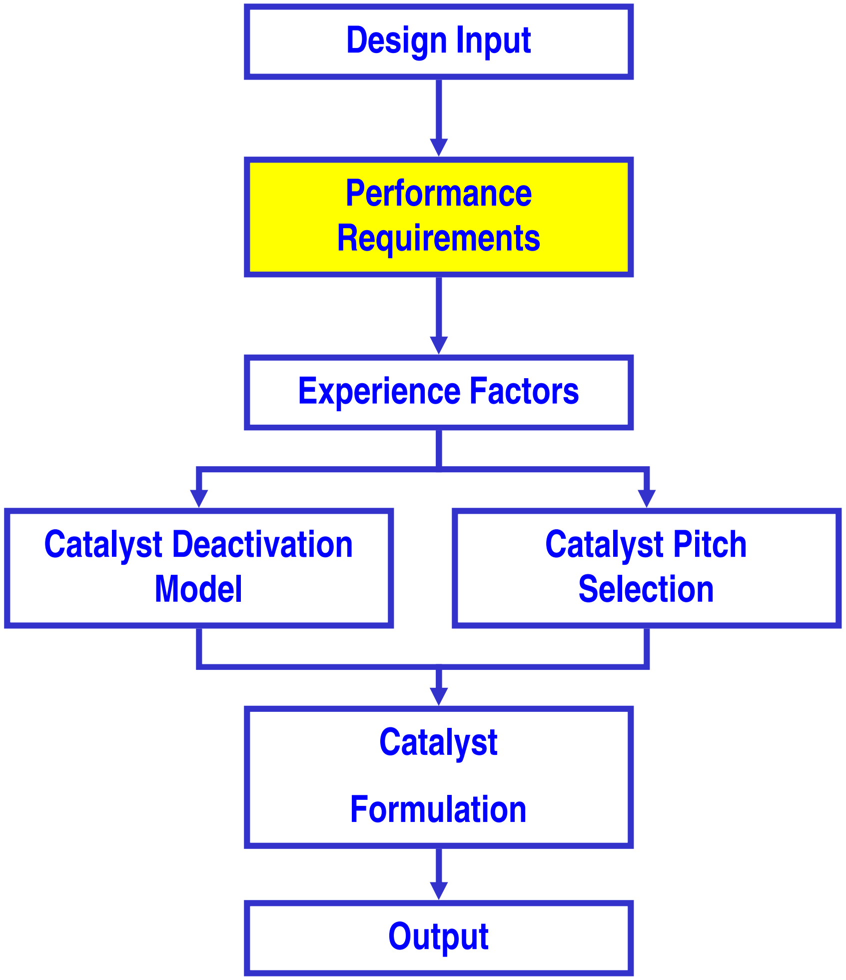


Design Inputs

- Flue Gas Flow Rate
- NOx Inlet
- Flue Gas Constituents
- Fuel Type & Analyses
- Reactor Size & Geometry
- Unit Type (PC, Cyclone, etc.)

Catalyst Design Process

CORMETECH

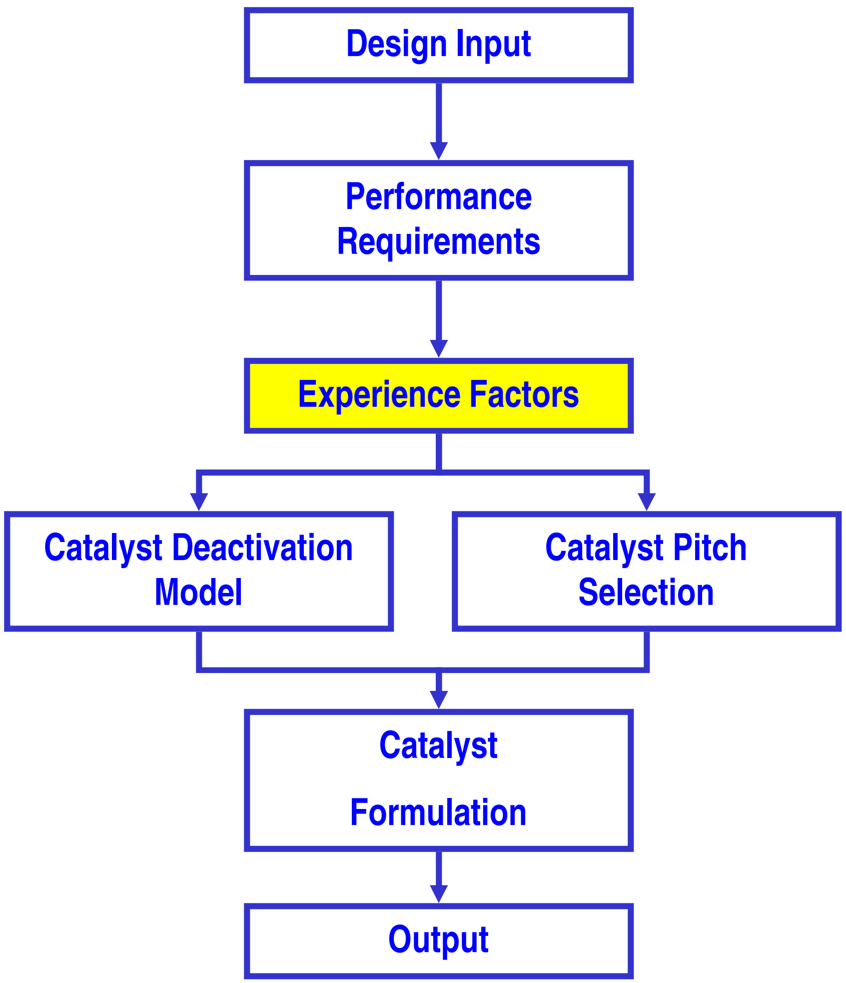


Performance Requirements

- NOx Removal Efficiency
- Ammonia Slip
- Pressure Drop
- SO_2 Oxidation Limit
- Initial Guaranteed Life

Catalyst Design Process

CORMETECH

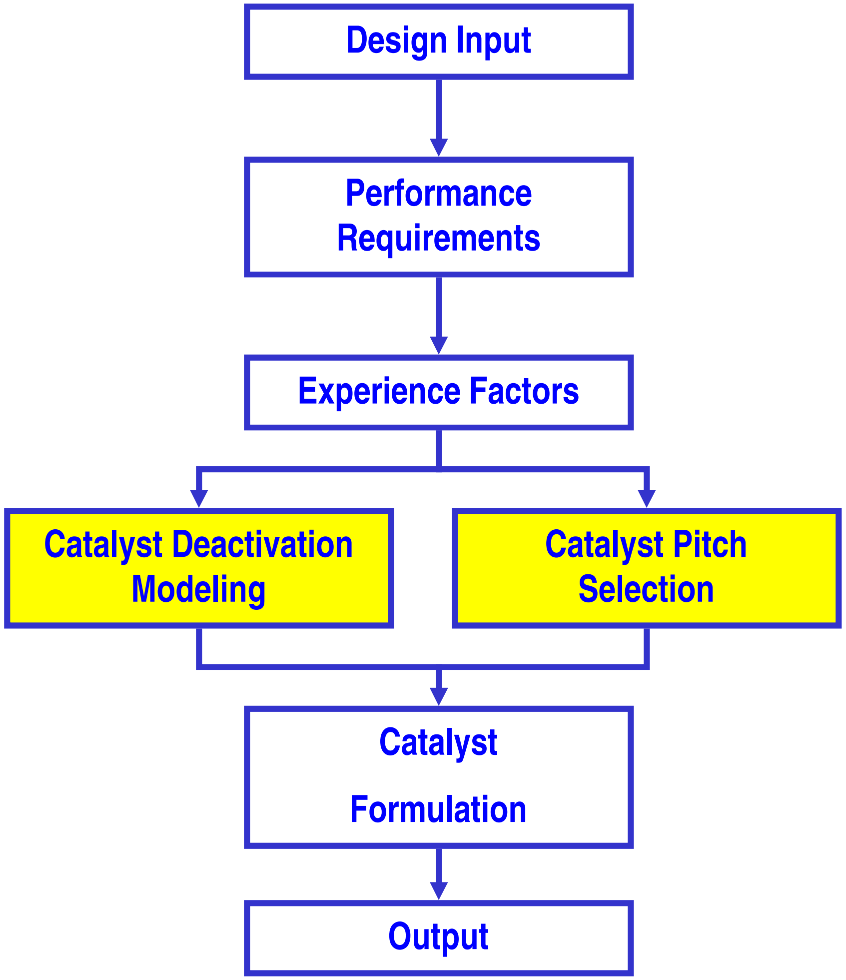


Experience Factors

- Catalyst Blockage
- Fouling / Plugging
- Maldistribution
  - NH_3 : NOx Molar Ratio
  - Temperature
  - Velocity

Catalyst Design Process

CORMETECH



Deactivation Modeling

- Fuels
- Unit Type
- Life Requirement

Catalyst Pitch Selection

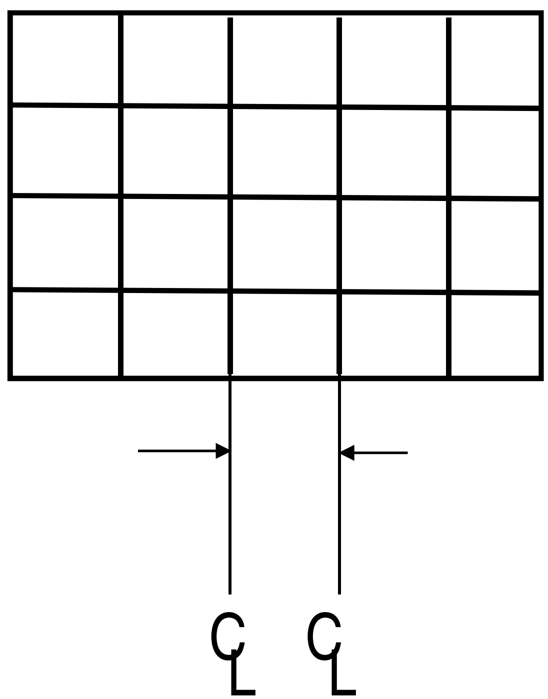
- Ash Characteristics
- Unit Type

Catalyst Description: Geometry

CORMETECH

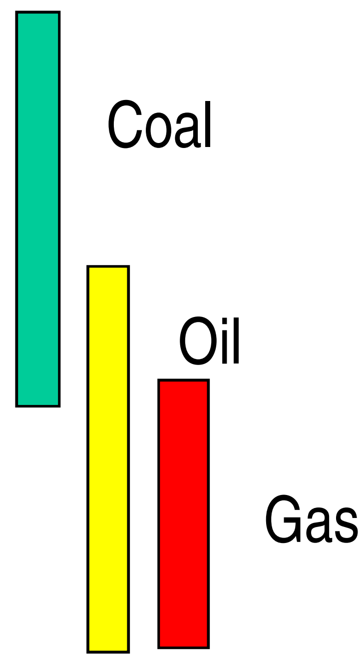
Catalyst pitch:

The distance from the center line of one catalyst wall to the center line of the next wall, or the cell opening plus one wall thickness



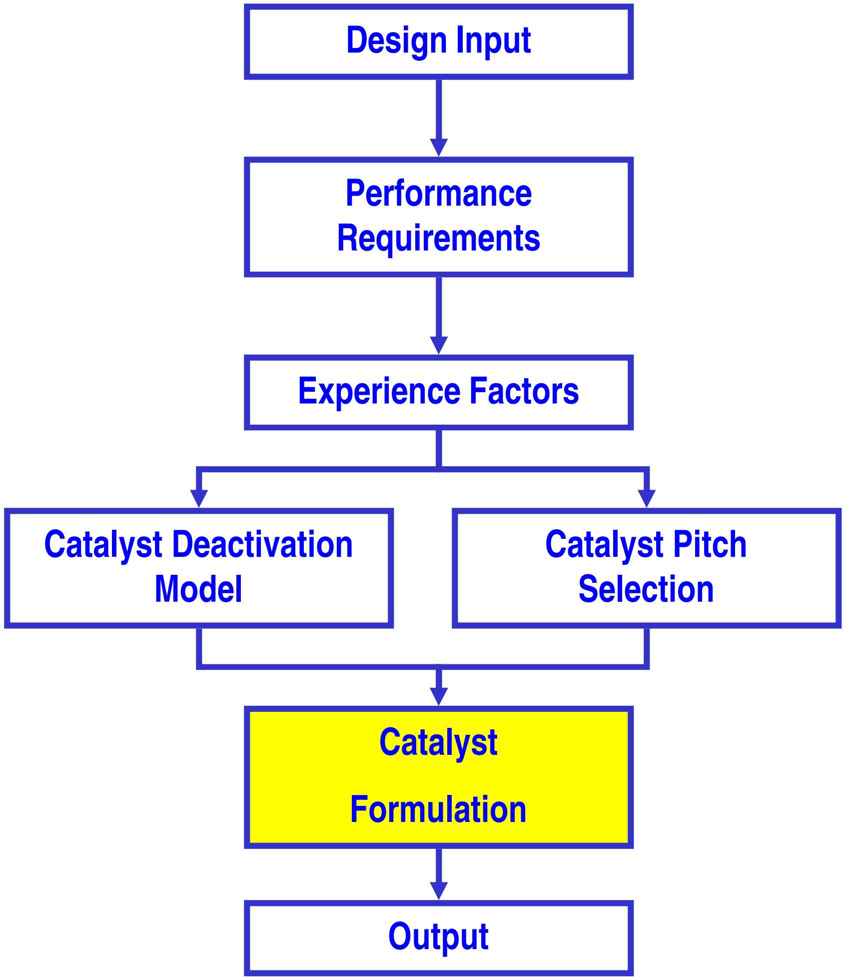
Pitch

- 9.2 mm = 16 cell
- 8.2 mm = 18 cell
- 7.4 mm = 20 cell
- 7.1 mm = 21 cell
- 6.9 mm = 22 cell
- 5.9 mm = 25 cell
- 4.2 mm = 35 cell
- 3.7 mm = 40 cell
- 3.3 mm = 45 cell
- 2.7 mm = 55 cell = 87 cpsi
- 2.1 mm = 70 cell = 140 cpsi



Catalyst Design Process

CORMETECH

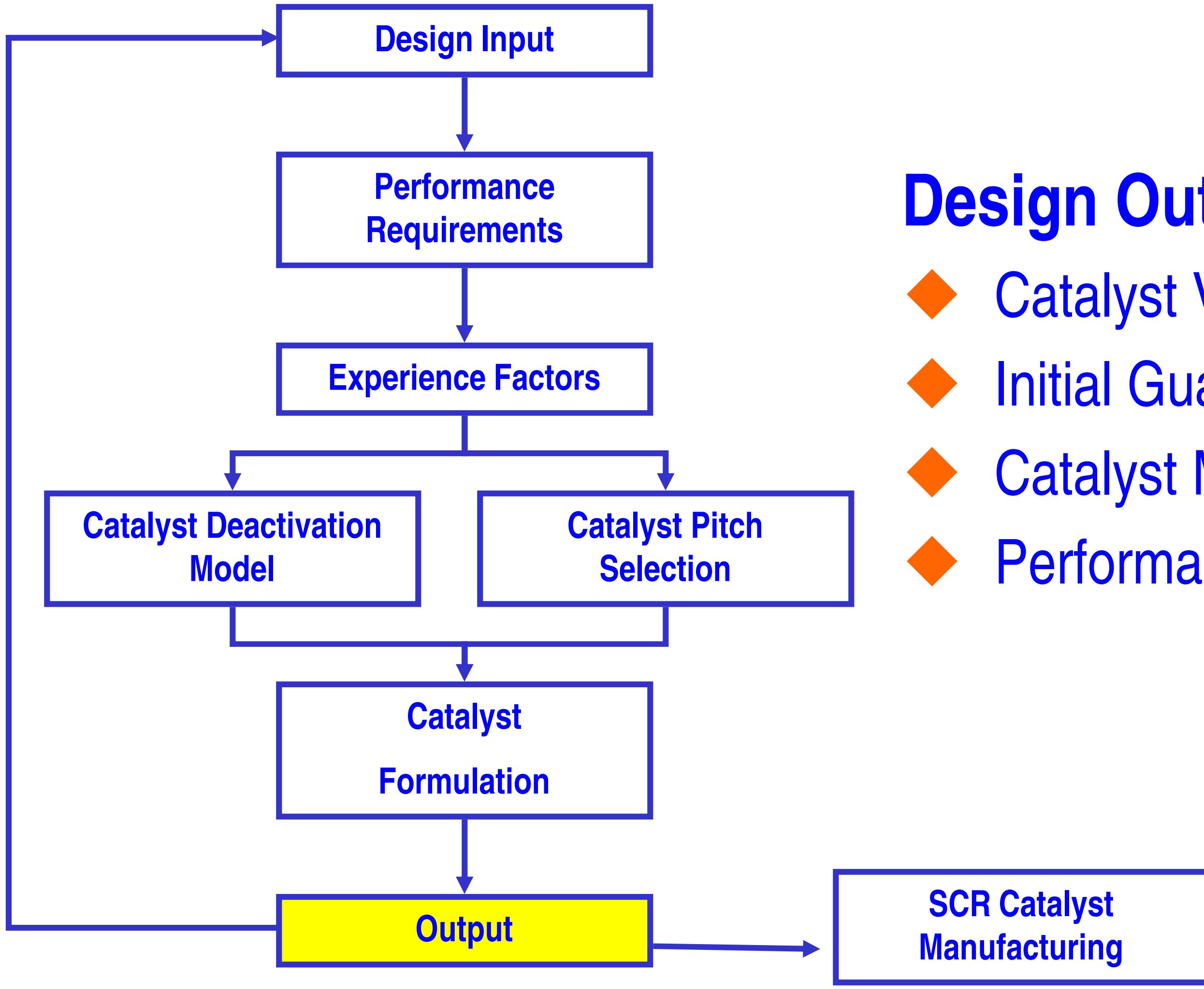


Catalyst Formulation

- Unit Type
- SO_2 Oxidation Limit
- Temperature Range

Catalyst Design Processs

CORMETECH



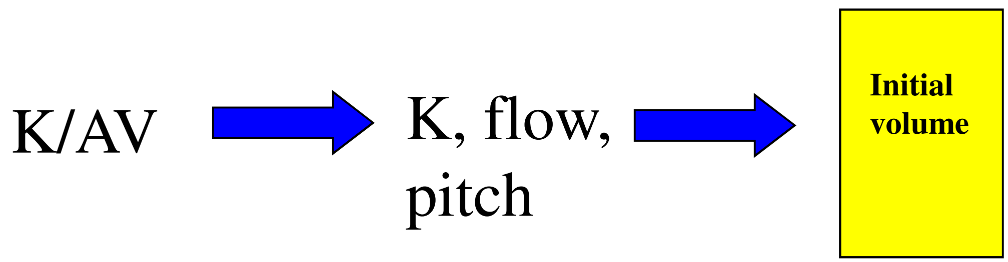
Design Output

- Catalyst Volume
- Initial Guaranteed Life
- Catalyst Management Plan
- Performance Criteria

Catalyst Requirements

CORMETECH

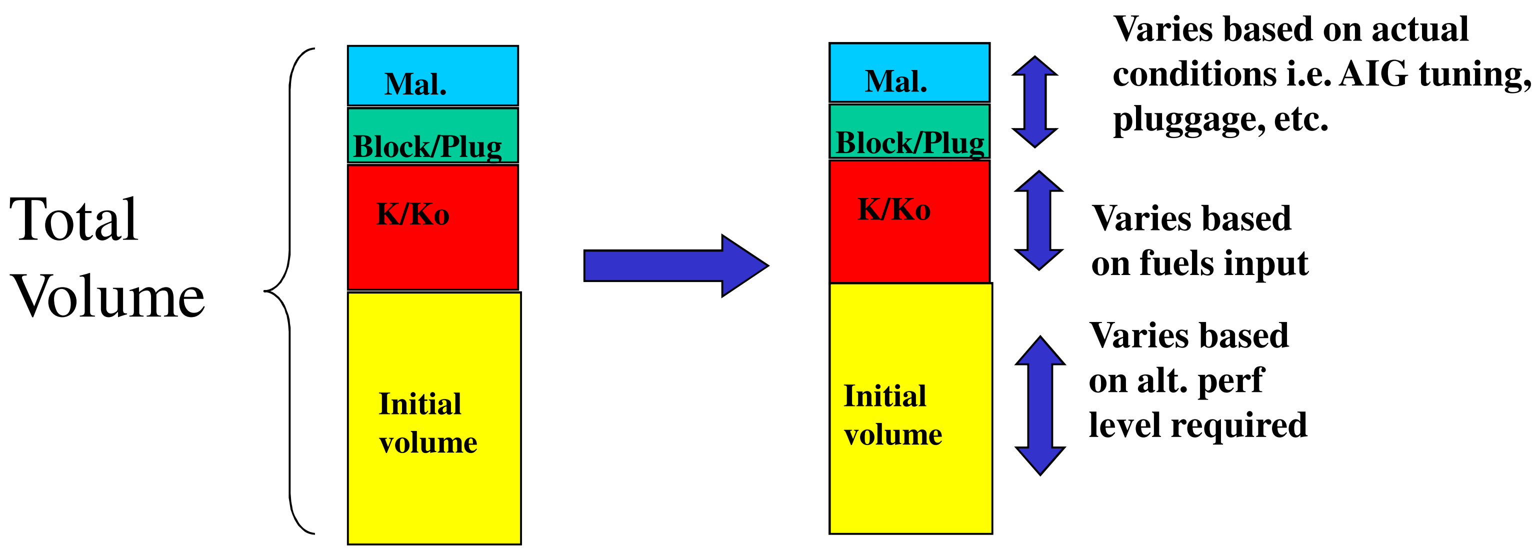
1. Determine minimum catalyst potential requirement K/AV = f(NOx in, efficiency, and NH_3 slip)
2. Determine initial catalyst activity K = f(T, form.)
3. Know flue gas flow (Nm^3/hr)
4. Select catalyst pitch and determine Geometric Surface Area (GSA)
5. Area Velocity, AV = flow Nm^3/hr / (Volume m^3 * GSA m^2/m^3)



Catalyst Requirements

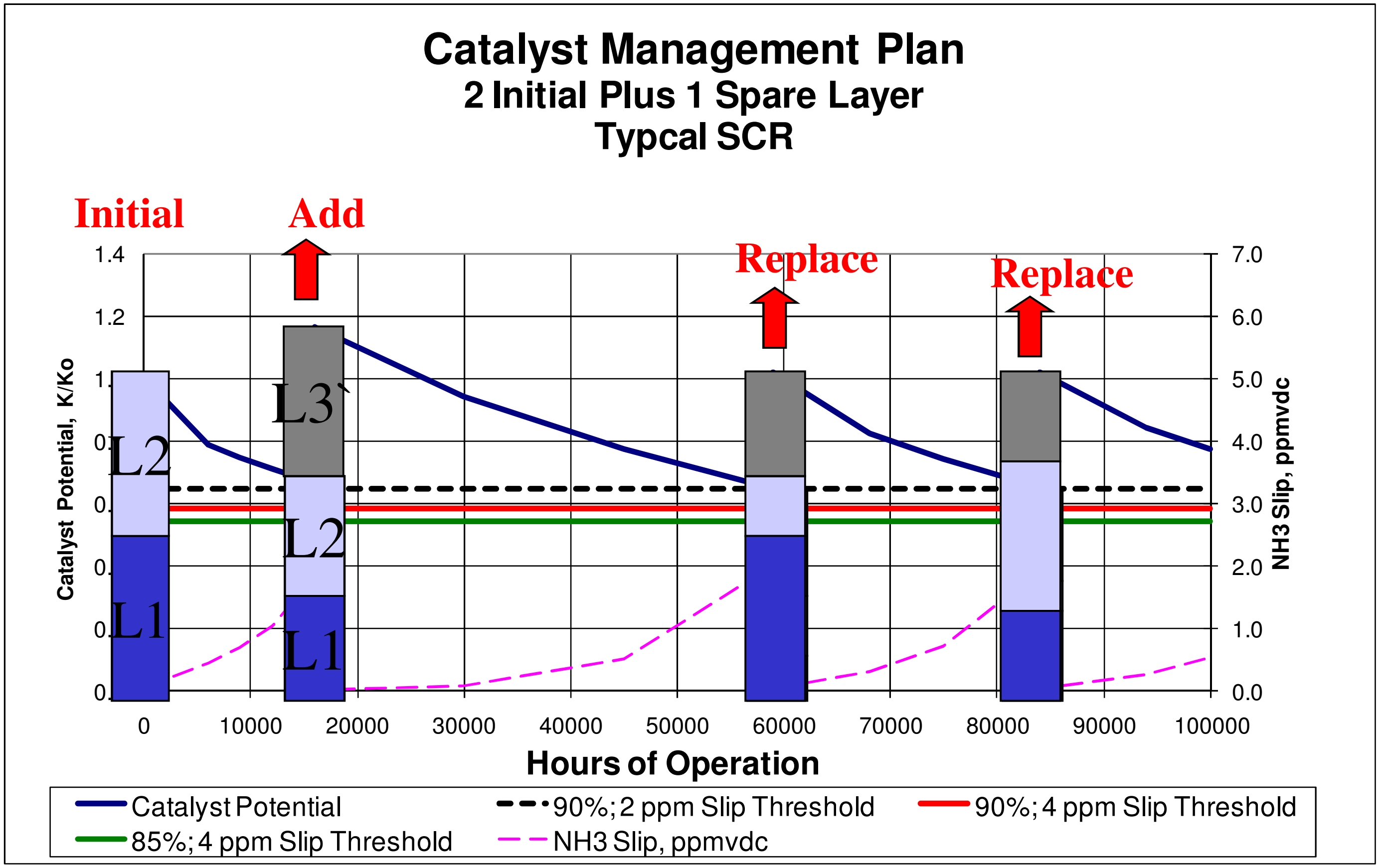
CORMETECH

6. Determine design margin required for
   - Fuels (K/Ko)
   - Blockage/pluggage
   - Maldistribution (NH_3:NOx, temperature, flow)
7. Iterate solution based on margin impact on formulation and K



Catalyst Management Plan

CORMETECH



SCR Operating Temperature

CORMETECH

- Operating temperatures
  - Minimum operating temperature for partial load conditions is determined by the formation temperature of ammonia sulfates
  - Maximum operating temperature is determined by the SO_2 oxidation requirements and module material limitations
  - Typically 600 – 800°F (320 – 425°C)

Ammonia Salt Formation

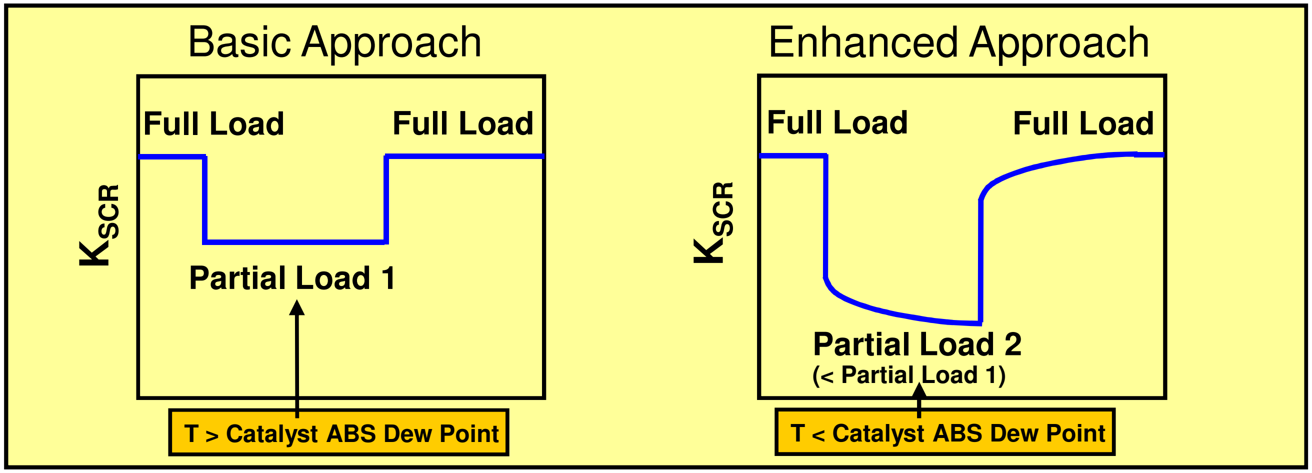
CORMETECH

- Ammonium bisulfate (ABS) deposition:
  - $NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \leftrightarrow NH_4HSO_{4(l)}$
- Liquid ABS can form in SCR catalyst pores at temperatures above the bulk phase dew point
- Typically minimum operating temperature limits prevent ABS formation

Low Temperature SCR Operation

CORMETECH

- **Enhanced Approach:**
  - Allows operation down toward the bulk ABS dew point
    - Controlled amount of ABS deposition and deactivation
    - Recover catalyst potential by reheating above recovery temperature
  - Evaluate: catalyst K/AV vs. performance requirement
    - Catalyst type and properties influence capability
  - Successfully implemented in >10 boilers



Additional Parameters

CORMETECH

- NH3 slip for individual coal-fired SCR applications vary:
  - Typically in the range of 2.0–5.0 ppmvdc at end-of-life
- Pressure drop is generally not a limiting factor in Coal fired applications:
  - The design pressure drop for coal-fired units is typically 0.7 – 1.2 in.wc. per layer
- Design life of SCR catalyst is usually measured in hours from first gas in:
  - The range of design life for coal-fired SCR catalyst depends on the requirements of the owner
  - Normally 8,000–24,000 hours from first gas in

CORMETECH

Catalyst Deactivation Mechanisms

Catalyst Deactivation Mechanisms
Catalyst Formulation/Sizing

CORMETECH

- Poisoning Potential.
  - CaO content.
  - As content.
  - Na, K content.
  - PSD.
  - Countermeasures.
    - Understand reaction.
    - Select appropriate catalyst formulation.
    - Account for in deactivation assumptions.
    - Fuel additives.

Catalyst Deactivation Mechanisms
Catalyst Formulation/Sizing

CORMETECH

- Fuel dependent.
  - Gas (Natural, Refinery).
  - Oil (Low Sulfur, High Sulfur, Particulate).
  - Coal (Low Sulfur, High Sulfur, CaO, As, Ash).
  - MSW (RDF, Mass Burn).
  - Biomass
- Application dependent.
  - Combustion turbine (Single cycle, Combined cycle).
  - Boiler (PC, Cyclone, CFB).

Catalyst Deactivation Mechanisms
Catalyst Formulation/Sizing

CORMETECH

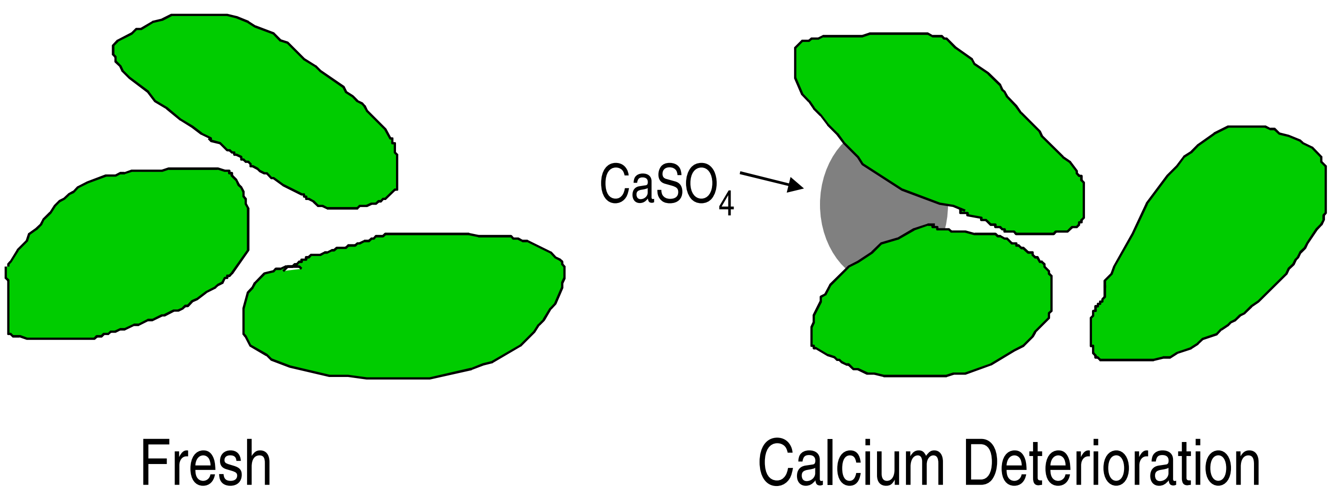
- Reduction of surface area.
  - Plugging or Masking catalyst surface.
    - Ca, Mg as sulfates and ammonium sulfate compounds.
    - Low temperature.
    - Particulates.
  - Chemical Bonding
    - As, Na, K.
  - Sintering.
    - High temperature operation > 800°F

Catalyst Deactivation Mechanisms

Calcium Oxide (CaO)

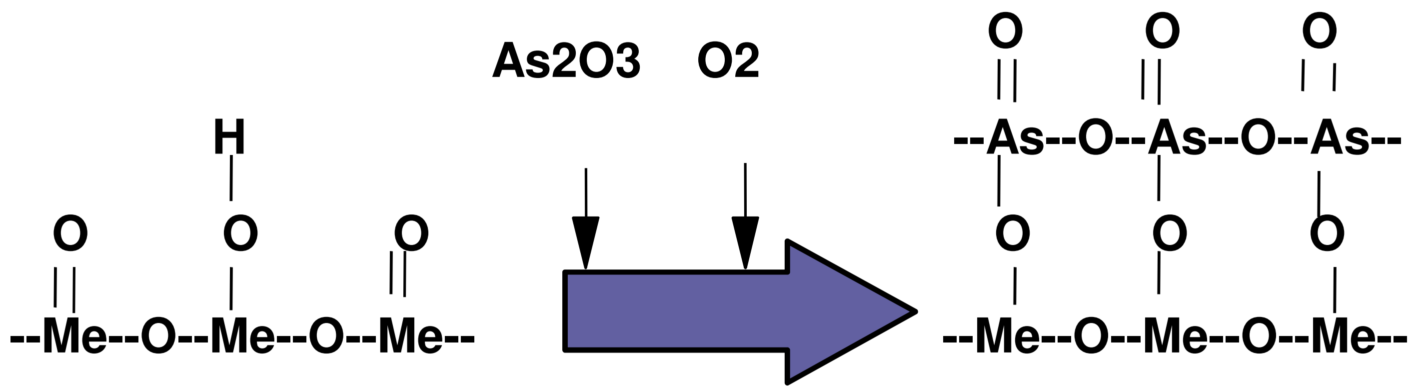
CORMETECH

- Alkaline Earth Metal (Ca, Mg).
  - Primarily Ca. CaO in flyash reacts with SO_3 to form $CaSO_4$. $CaSO_4$ causes catalyst surface pore plugging (typically ~5 micron depth).



Catalyst Deactivation Mechanisms
Arsenic (As)

- Gaseous arsenic, As_2O_3, diffuses into the catalyst wall and covers active sites. At SCR inlet, gaseous As is typically 5% of total As in flue gas stream.

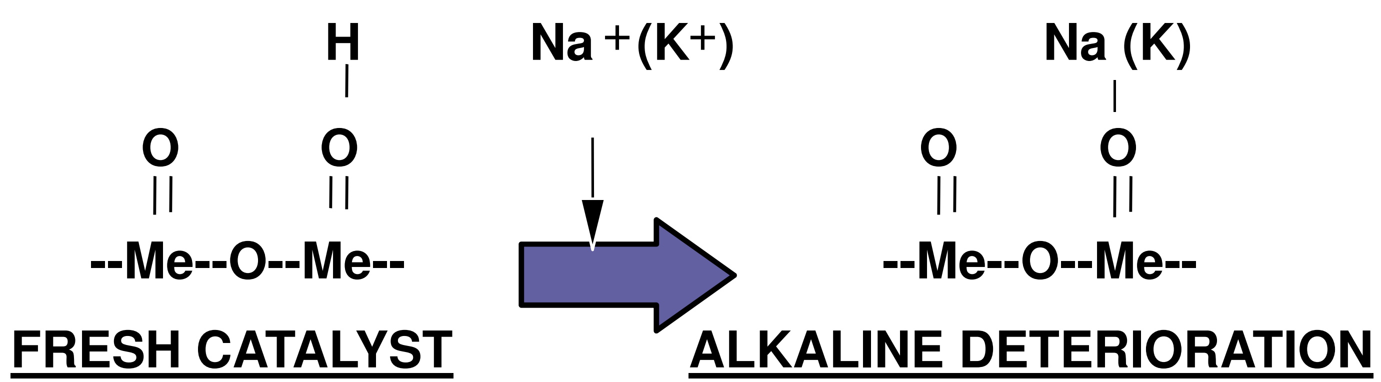


Catalyst Deactivation Mechanisms

CORMETECH

Alkaline Metal (Na/K)

- Exist in the dust as sulfates, Na_2SO_4 and K_2SO_4, readily soluble in water. The alkaline ion moves freely through the catalyst wall and bonds with acid sites resulting in decreased capability to adsorb ammonia thus decreasing catalyst potential.



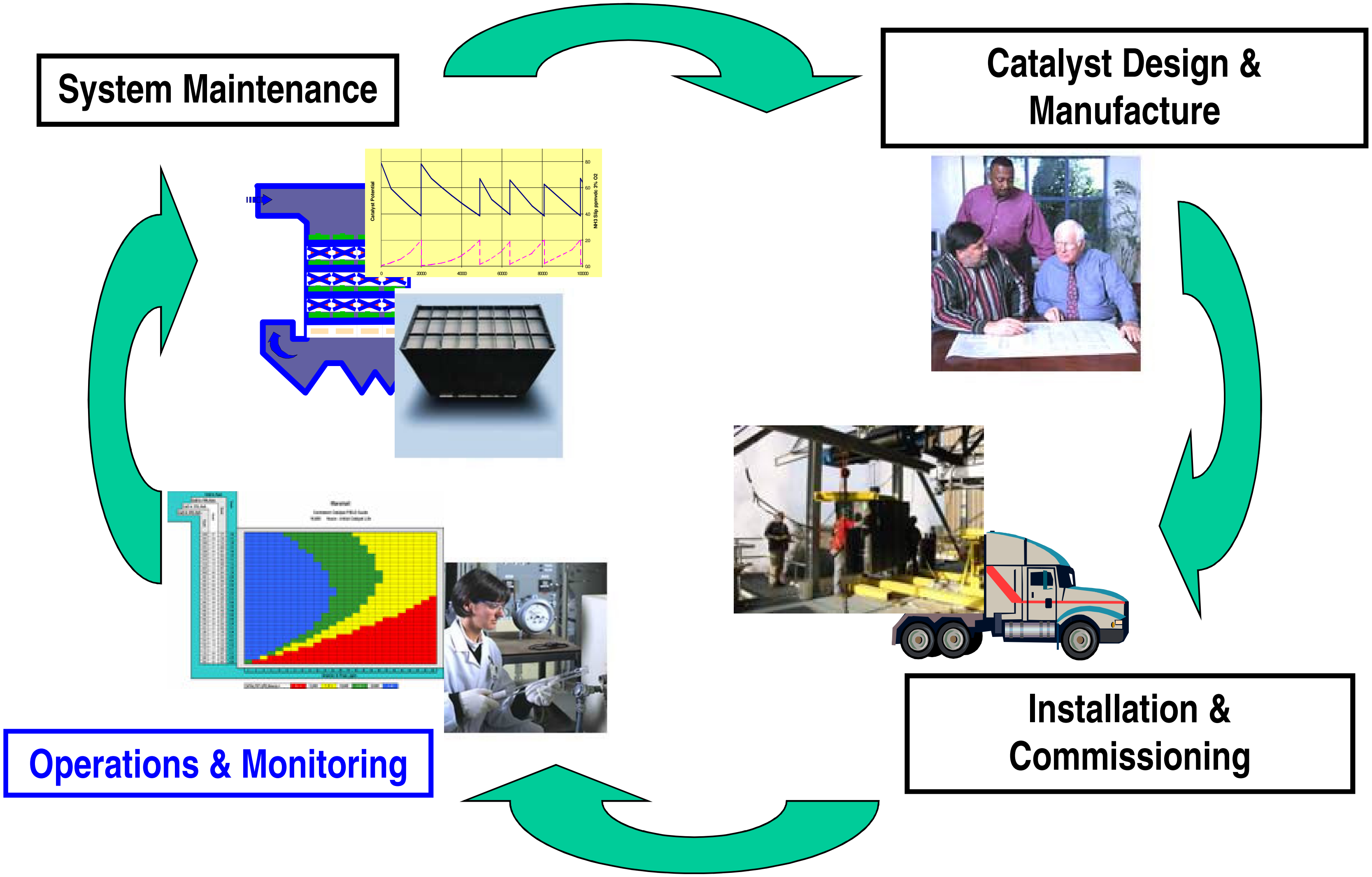
Catalyst Deactivation Mechanisms

CORMETECH

- Vanadium (V).
  - Can have positive effect on catalyst DeNOx performance. However, causes higher SO_2 oxidation which degrade overall performance and may lead to downstream equipment fouling.
- Thermal Degradation.
  - Primary means of gas catalyst deterioration.
  - Sintering causes decrease in pore volume and surface area.

Catalyst Life-Cycle Management

CORMETECH



Operation & Monitoring

CORMETECH

- Fuels monitoring
- Performance monitoring
- NH_3 in ash
- SCR Inspections
- Catalyst testing
- AIG tuning/distribution measurement

Operation & Monitoring

CORMETECH

- Fuels monitoring
  - Create fuel sampling plan:
    - Used to monitor catalyst deactivation in between catalyst testing.
    - Fuel analysis on weekly/monthly basis depending upon expected variability / number of coals fired
    - Analysis must include the following items:
      - Sulfur, %
      - Ash in fuel - % (as received)
      - Arsenic in Coal, ppm
      - Calcium oxide in ash - % (Free and total)
- Monitor impact of fuels with FIELD guide
    - Life estimation by FIELD guide
    - More detail by CM model

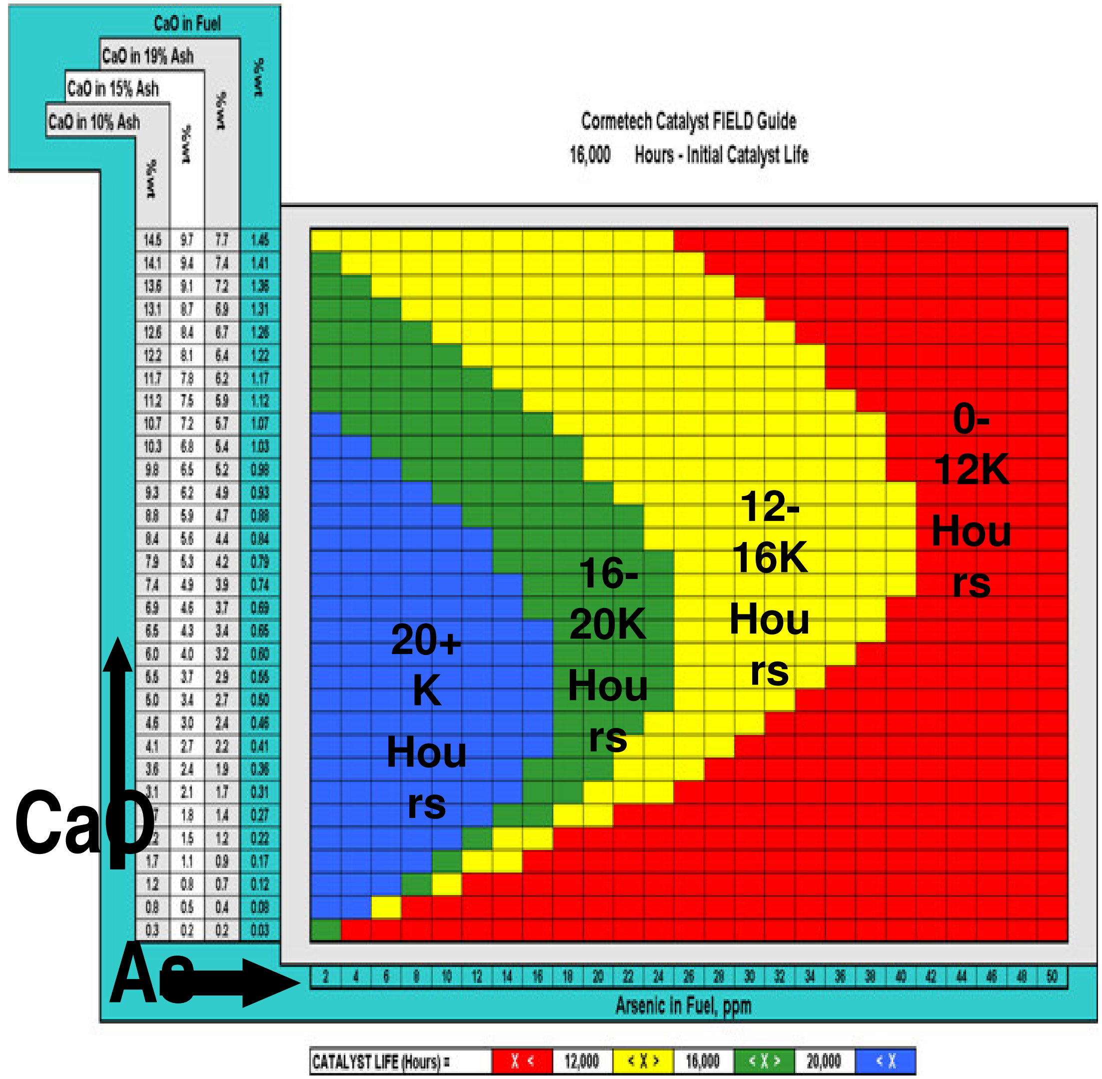
FIELD guide

CORMETECH

For **F**uel **I**mpact **E**valuation & **L**ife **D**etermination

Estimates catalyst life for a defined coal-fired boiler SCR

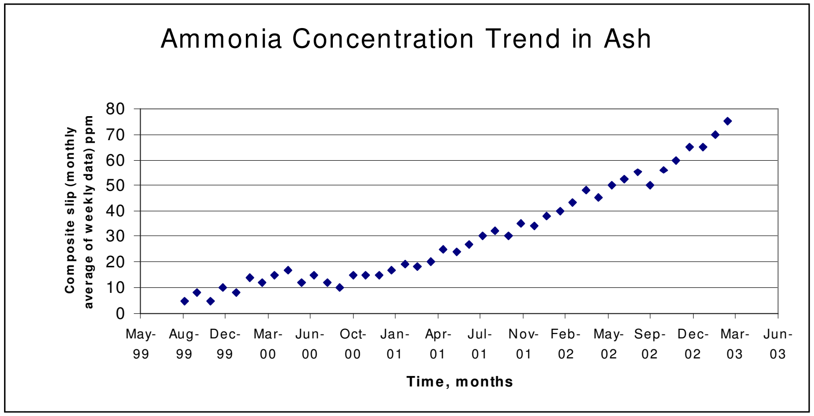
- Uses arsenic (As) and calcium oxide (CaO) fuel content
- Assumes all other variables are constant.



Operation & Monitoring

CORMETECH

- Evaluation of NH_3 in ash results
  - Indicates when system needs attention
  - Surrogate of NH_3 slip
  - NH_3 testing in ash
    - Daily to weekly basis
    - Consistent sample location
    - Test methods
    - Sensitive to high fuel variability
    - Repeatable process
  - Plot and evaluate results



Catalyst System Inspection

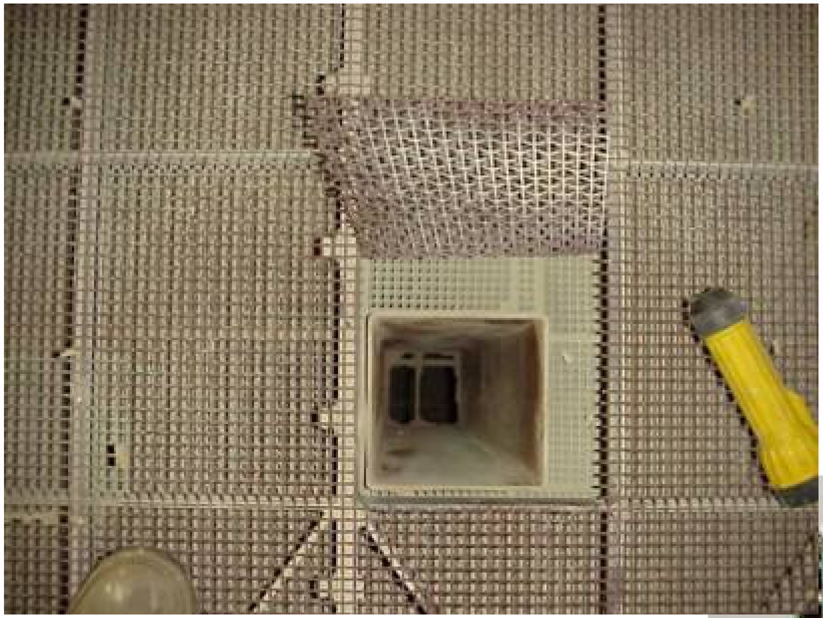
CORMETECH

- Sealing
- Plugging
- Erosion
- Sonic Horn / Sootblower effectiveness

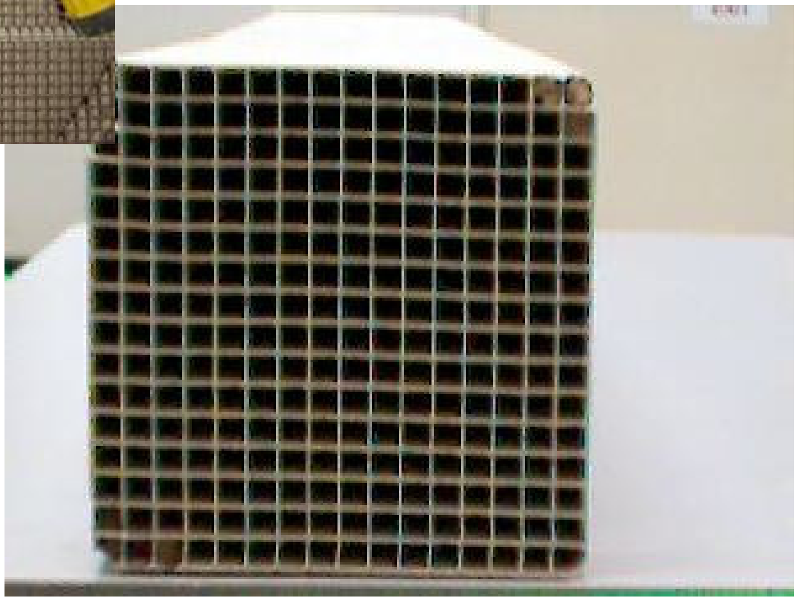
Sampling done in conjunction with inspection

Catalyst Sampling

CORMETECH



Full-size sample elements are removed and tested in Cormetech's laboratory

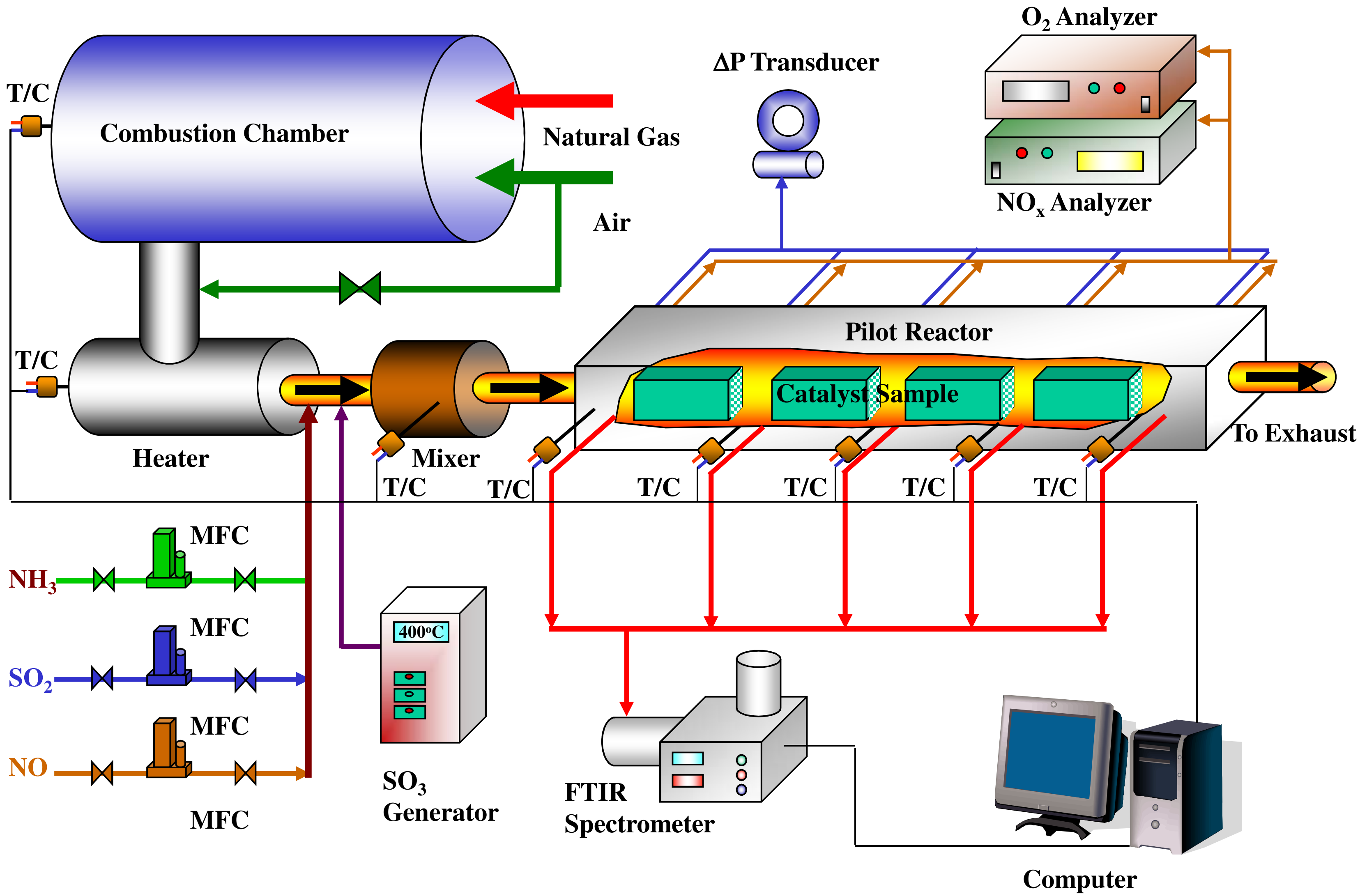


Catalyst Analytical Strategy

CORMETECH

- Pilot tests to determine K_o (initial activity) for the catalyst design
- Pilot tests for field samples to determine K_t (activity at time t) for used catalysts materials
- Comparison of K_t/K_o with design expectations
- Analytical techniques utilized for
  - Surface analysis
  - Bulk analysis from a percent to part per billion
  - Depth profiling of contaminants

Pilot Test Plant



Cormetech, Inc Pilot Reactor Schematic

Auditing of field catalyst elements at *actual* operating conditions

Catalyst Analytical Strategy

CORMETECH

- Engineering analysis of fuels, process conditions
- Physical inspection of catalyst samples
- Bulk and surface analysis techniques
  - Inductively Coupled Plasma Mass Spectrometry (ICP)
  - X-Ray Fluorescence Spectroscopy (XRF)
  - Scanning Electron Microscopy with Energy Dispersive X-ray Analyzer (SEM/EDXS)
  - X-ray Photoelectron Spectroscopy (XPS/ESCA)
  - Secondary Ion Mass Spectrometry (SIMS)
  - Porosity and Surface area

Basic Catalyst Sample Processing Steps

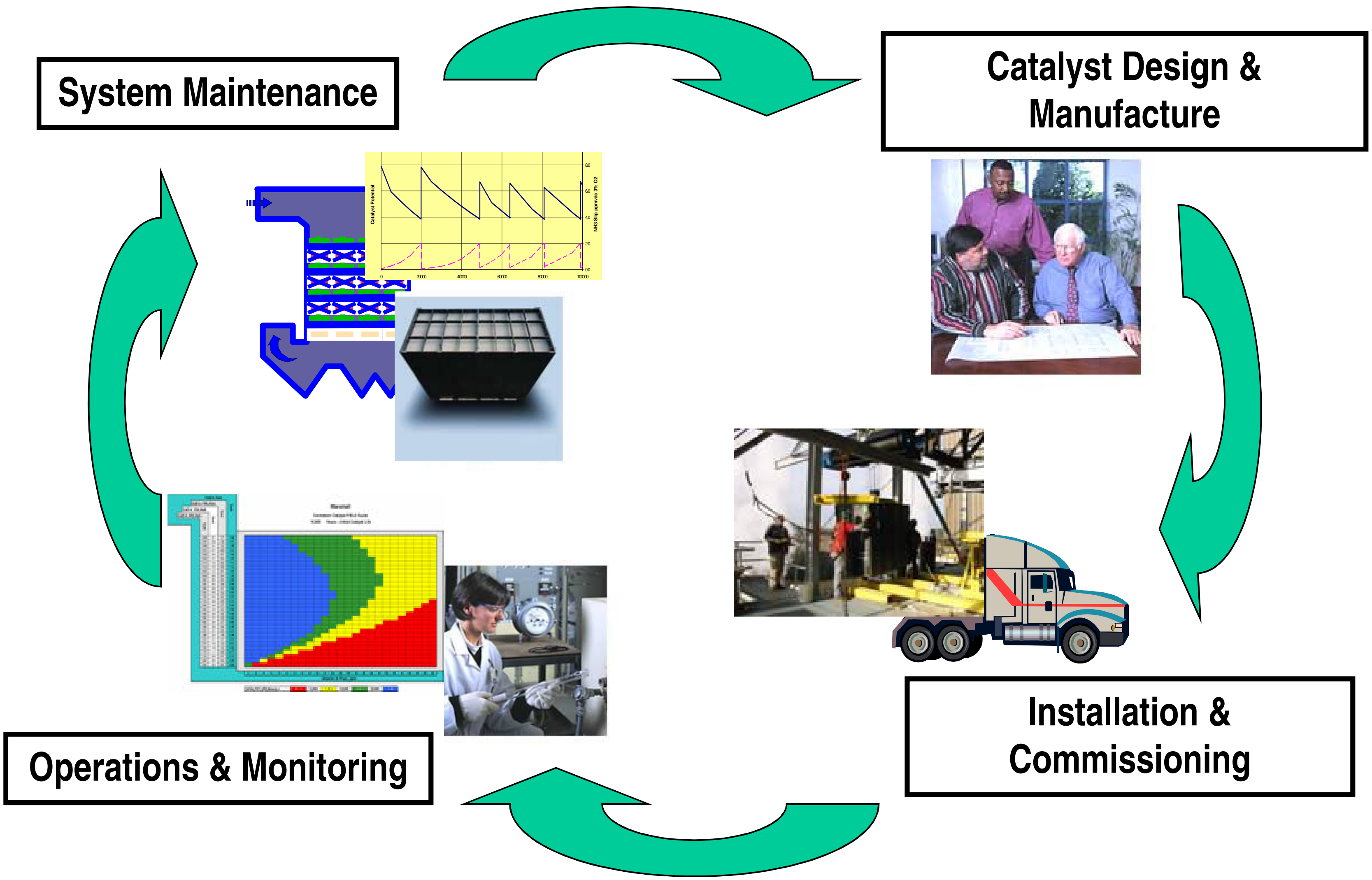
CORMETECH

- Visual inspection
- Specification of appropriate test conditions/requirements
- Sample preparation
  - Chemical composition (catalyst, deposit)
  - Porosity, surface area, etc.
  - Pilot test
- Testing
- Results and analysis
- Comparison to expectations based on field data
- Report including recommendations

- Additional considerations
  - Engineering services to extend catalyst life
    - Performance requirements
      - Efficiency
      - Inlet NOx
      - Ammonia slip
    - Fuel changes

Catalyst Life-Cycle Management

CORMETECH



CORMETECH

End of Presentation….

Thank you for your attention…

Questions?