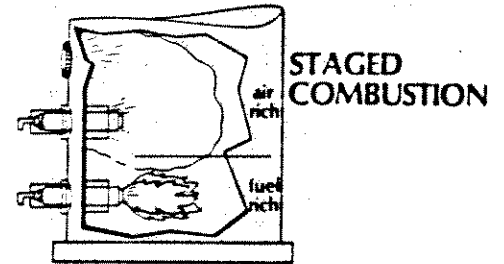
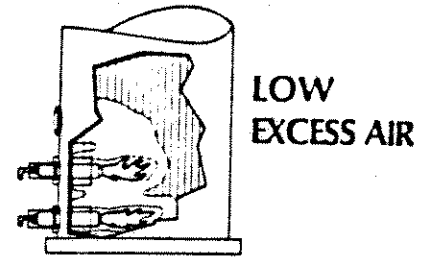
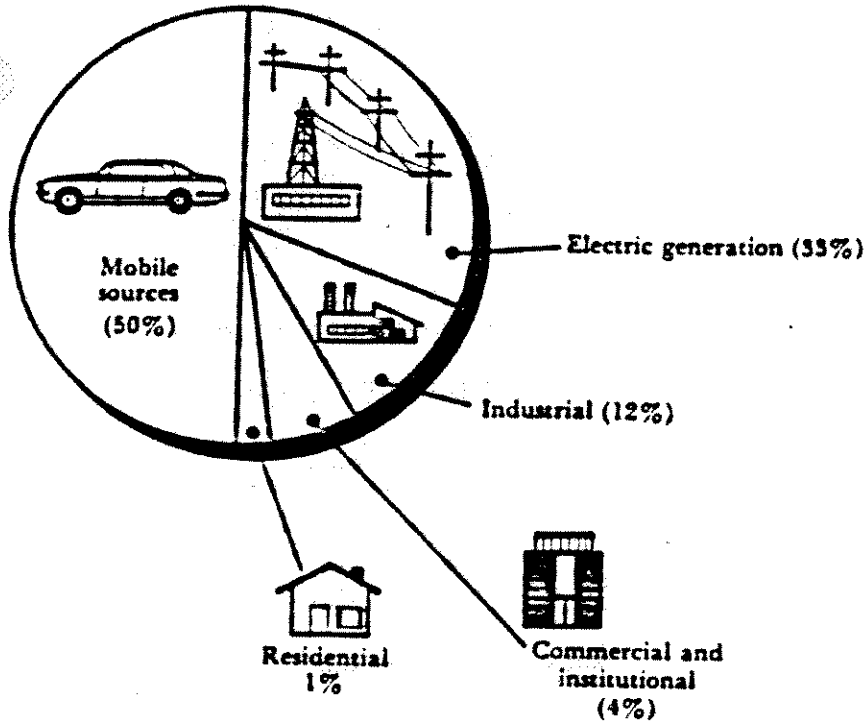
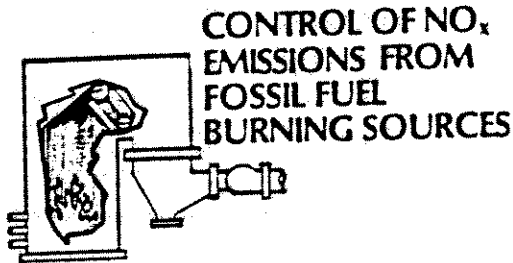


# Control of Nitrogen Oxide Emissions

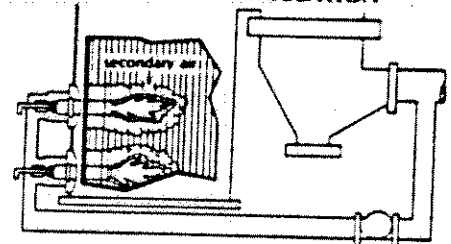


## STAGED COMBUSTION TECHNIQUES

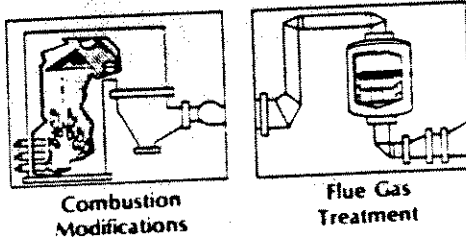
- Overfire Air Ports
- Burners Out Of Service
- Air/Fuel Mixing



## FLUE GAS RECIRCULATION



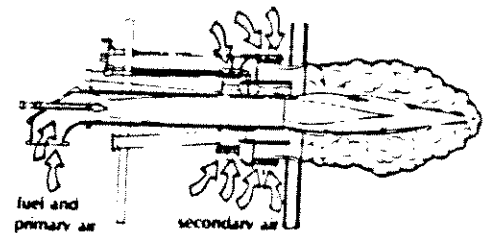
## METHODS OF REDUCTION



## COMBUSTION MODIFICATIONS

- Low Excess Air
- Staged Combustion
- Flue Gas Recirculation
- Low NO<sub>x</sub> Burners

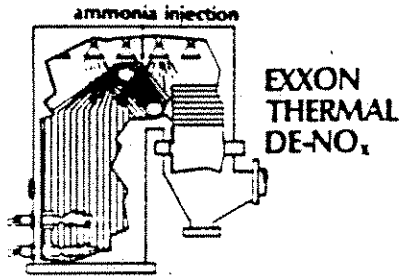
## LOW NO<sub>x</sub> BURNER



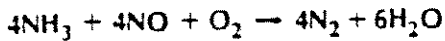


## FLUE GAS TREATMENT

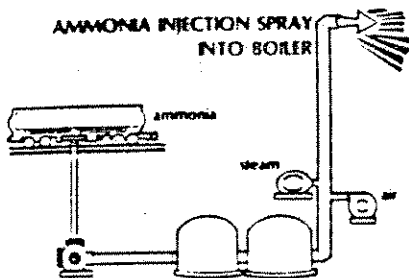
- Exxon Thermal De-NO<sub>x</sub>
- Selective Catalytic Reduction (SCR)
- UOP Shell Process
- Wet NO<sub>x</sub>/SO<sub>x</sub> Process



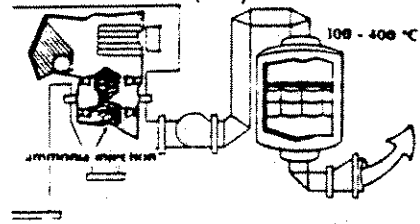
## THERMAL DE-NO<sub>x</sub> PROCESS CHEMISTRY



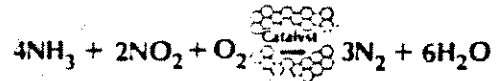
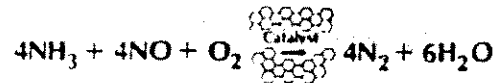
- Required Flue Gas Temperature — 950 °C  
(If hydrogen injected — 700 °C)



## SELECTIVE CATALYTIC REDUCTION (SCR)



## SCR PROCESS CHEMISTRY



Metal Honeycomb



Parallel Plate

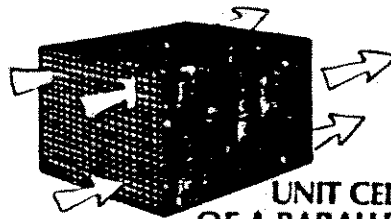


Tubular

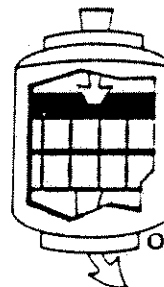
## SHAPES OF PARALLEL FLOW CATALYSTS



Ceramic Honeycomb



UNIT CELL OF A PARALLEL FLOW CATALYST



## TYPICAL PARALLEL FLOW CATALYTIC REACTOR

Optimum Flue Gas Temperature  
300 - 400 °C

## Natural Gas Fueled Gas Turbine NO<sub>x</sub> Exhaust Gas Concentrations

**Given:** The exhaust gases from a gas turbine plant (burning natural gas) has the following composition at 1.0 atm. pressure:

74.0% N<sub>2</sub>  
 16.0% O<sub>2</sub>  
 3.6% CO<sub>2</sub>  
 6.4% water vapor at 1,340°F or 999.66°K

Molecular wt of NO = 30.01

$$C_{\text{NO}_x}(\text{corrected to } 15\% \text{ O}_2) = \left\{ \frac{20.9 - 15\% \text{O}_2}{20.9 - \text{Stack Gas } \% \text{O}_2} \right\} (\text{stack gas } C_{\text{NO}_x})$$

New Source Perf. Std. for Gas Turbines = 0.2 lb NO<sub>x</sub> per million Btu heat input (pp 77 WW&D)

F<sub>d</sub> = 8740 ft<sup>3</sup> gas emitted per million Btu heat input for nat. gas combustion

$$E \frac{\text{lb NO}_x}{10^6 \text{ Btu Heat Input}} = \left( \text{NO}_x \frac{\text{lb}}{\text{ft}^3} \right) \left( F_d \frac{\text{ft}^3}{10^6 \text{ Btu Heat Input}} \right) \left( \frac{20.9}{20.9 - \text{O}_2 \text{Dry}} \right)$$

where O<sub>2</sub>Dry is the % oxygen in the gases on dry basis (i.e. 0% water vapor)

**Find:**

a. Conc of NO in exhaust gases corresponding to the 0.2 lb/10<sup>6</sup> Btu NSPS allowed emission  
 \_\_\_\_\_ ppm NO dry corrected to 15.0% dry O<sub>2</sub>

b. Will the NO equilibrium conc. @ 1,340°F calc. meet the NSPS EPA standards?

In other words, there is an equilibrium reaction  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO}$

The equilibrium constant K<sub>p</sub>  $K_p = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 7.5 \times 10^{-9}$  at 1,340°F

This K<sub>p</sub> is from Table 8-4 pp 435. [NO] is the NO concentration.

Note that the NO, N<sub>2</sub>, and O<sub>2</sub> need to all be in the same concentration units.

One can use this relationship to calculate the NO equilibrium concentration using the known K<sub>p</sub>, N<sub>2</sub> conc. of 74.0% and O<sub>2</sub> conc. of 16.0% (these are wet basis concentrations).

(see pages 434-446 WW& Davis for discussion of NO and NO<sub>2</sub> formation)

## NOx Exhaust Gas Concentrations and Emission Standards Gas Turbine burning natural gas as fuel

Exhaust Gases of 74% N<sub>2</sub>, 16% O<sub>2</sub>, 3.6% CO<sub>2</sub>, and 6.4% water vapor T=1,340 Deg F

### a. Concentration of NO corresponding to NSPS of 0.2 lb NOx/million Btu Heat Input

EPA Federal Emission Standards for Gas Turbines were established in 1979 for NOx and SO<sub>2</sub>  
NSPS = 0.2 lb NOx per million Btu heat input = E Fd = 8740 cubic ft gas / million Btu Heat input

$$E := 0.2 \cdot \left( \frac{\text{lb}}{1000000 \cdot \text{BTU}} \right) \quad \text{Cd} = \text{NOx conc., lb NOx / dscf} \quad \text{O2Dry} = \text{oxygen conc., \% by vol., dry} \quad \text{Fd} := 8740 \cdot \left( \frac{\text{ft}^3}{1000000 \cdot \text{BTU}} \right)$$

$$\text{O2Dry} := 15.0$$

$$E := (\text{Cd}) \cdot (\text{Fd}) \cdot \left( \frac{20.9}{20.9 - \text{O2Dry}} \right) \quad \text{Cd} := \frac{E}{\left( 8740 \cdot \frac{\text{ft}^3}{1000000 \cdot \text{BTU}} \right) \cdot \left( \frac{20.9}{20.9 - \text{O2Dry}} \right)}$$

$$\text{Cd} = 6.45987759 \cdot 10^{-6} \cdot \frac{\text{lb}}{\text{ft}^3}$$

Vol. 1 lb mole @ 68 deg F = (359) (528R/492R) = 385.2683 cubic ft

Conversion Factor = (30.01 lb/mole) / [(385.2683 cf/mole) (million)] = 7.7894 E-8 (lb/cf)/(ppm NO)

$$\text{ppm} := \frac{\left( \frac{\text{Cd}}{\text{lb}} \right)}{7.7894 \cdot 10^{-8}}$$

NSPS allowed NO conc.  
corrected to 15.0% oxygen = ppm = 82.93164545

NSPS allowed Emission NO Conc. corrected to 15.0% Oxygen = 82.9316 ppm

### b. Calc. of NO Equilibrium Conc. at 1,340 Deg. F or 999.66 Deg K @ Kp = 7.5 x 10<sup>-9</sup> pp 435

WW&Davis

Using gas conc. on a wet basis

$$K_p := \frac{\text{NO}^2}{(\text{N}_2) \cdot (\text{O}_2)}$$

$$\text{N}_2 := 74.0\% \quad \text{O}_2 := 16.0\% \quad K_p := 7.5 \cdot 10^{-9}$$

Solving for NO

$$\text{NO} := \left[ (7.5 \cdot 10^{-9}) \cdot (74.0\%) \cdot (16.0\%) \right]^{0.5}$$

$$\text{ppm} := .0001\% \quad \text{NO} = 2.979933 \cdot 10^{-3} \cdot \% \quad \text{NO} = 29.79932885 \cdot \text{ppm}$$

NO Equil. Conc. at 1,340 Deg F, 6.4% water vapor, & 16% oxygen = 29.80 ppm

Correct from NO wet to NO dry concentration & at 15.0% Oxygen

$$\text{NOWet} := 29.79933 \cdot \text{ppm}$$

$$\text{BWS} := 0.064$$

$$\text{NOdry} := \frac{\text{NOWet}}{(1 - \text{BWS})}$$

BWS = fractional Conc. water vapor

$$\text{O2wet} := 16.0\%$$

$$\text{NOdry} = 31.83689103 \cdot \text{ppm}$$

$$\text{O2dry} := \frac{\text{O2wet}}{(1 - \text{BWS})}$$

$$\text{O2dry} = 17.09401709 \cdot \%$$

$$\text{Diff} := 20.9 - 17.09401709$$

$$\text{NOcorrected} := (\text{NOdry}) \cdot \left( \frac{5.9}{\text{Diff}} \right)$$

$$\text{Diff} = 3.80598291$$

NO Corrected to 15% Oxygen

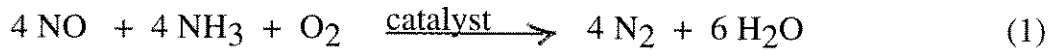
$$\text{NOcorrected} = 49.35325814 \cdot \text{ppm}$$

NO Equil. conc. dry @ 15.0% Oxygen = 49.35 ppm by gaseous volume

Thus NO Equilibrium Conc of 49.35 ppm will meet NSPS of 82.93 ppm NO corr. to 15% O<sub>2</sub>  
This implies that NSPS is not a very restrictive emission std (which is typical for EPA NSPS).  
Note that new installations must meet EPA BACT, not merely NSPS.

## Selective Catalytic Reduction of NO<sub>x</sub> by M. Pilat (3/9/98)

Given: Principal Chemical Reactions



Cylindrical tube of Catalyst of Diameter D and Length L inside a honeycomb matrix

The NO<sub>x</sub>, NH<sub>3</sub>, and O<sub>2</sub> diffuses to the inside surface of the cylindrical tube catalyst and is assumed to react quickly (i.e. reaction rate constant  $k_r =$  extremely large number). In the easiest first case, it can be assumed that the reaction rate is so fast (i.e.  $k_r =$  very large compared to  $k_m$ ) that the reaction of the NO or NO<sub>2</sub> with the NH<sub>3</sub> is limited by the rate of mass transfer (diffusion) to the catalyst surface. The pressure drop from the tube inlet to outlet is small (less than 3" H<sub>2</sub>O) and hence the gas velocity is assumed to be constant in the x or L direction.

The nomenclature is as follows:

C	= concentration of the NO in the air	gms NO/cm <sup>3</sup>
a	= surface area of catalyst / unit volume of reactor	cm <sup>2</sup> /cm <sup>3</sup>
D	= effective diameter of the tube of channel	cm
K <sub>o</sub>	= overall mass transfer coefficient	cm/sec
k <sub>m</sub>	= mass transfer coefficient	cm/sec.
k <sub>r</sub>	= reaction rate constant of NO with NH <sub>3</sub>	cm/sec
L	= Length of the catalyst reactor channel	cm
L <sub>m</sub>	= Length of one mass transfer unit	cm
N	= Number of mass transfer units	
v	= velocity of the gas in the catalyst tube	cm/sec
∅	= diffusion coefficient of NO in air	cm <sup>2</sup> /sec

The change in the NO concentration down the tube caused by the diffusion to the wall and catalytic reduction to N<sub>2</sub> and H<sub>2</sub>O is given by the equation

$$\frac{dC, \frac{\text{gm NO}}{\text{cm}^3}}{dx, \text{cm}} = - \frac{\left( a \frac{\text{cm}^2 \text{ area}}{\text{cm}^3 \text{ volume}} \right) \left( K_o \frac{\text{cm}}{\text{sec}} \right) \left( C \frac{\text{gm NO}}{\text{cm}^3} \right)}{(v, \text{cm} / \text{sec})} \quad (3)$$

Rearranging equation 3  $\frac{dC}{C} = - \frac{(a)(K_o) dx}{v}$  (4)

and integrating from the tube inlet (  $x = 0$  and  $C = C_o$  ) to some distance  $x$  (where  $x = x$  and the NO conc. is  $C$  )

$$\int \frac{dC}{C} = - \int \frac{(a)(K_o)}{v} dx \quad (5)$$

The results of the integration are

$$\ln C - \ln C_o = \ln \frac{C}{C_o} = - \frac{(a)(K_o)(x)}{v} \quad (6)$$

$$\frac{C}{C_o} = \exp \left( - \frac{a K_o x}{v} \right) \quad (7)$$

With no vapor pressure of NO over the catalyst surface, number of mass transfer units is given by

$$N = \ln \left( \frac{C_{\text{inlet}}}{C_{\text{outlet}}} \right) \quad (8)$$

For one mass transfer unit,  $N = 1 = \ln [ C_{\text{inlet}} / C_{\text{outlet}} ]$  (9)

$$e^1 = (C_{\text{inlet}} / C_{\text{outlet}}) \quad e^{-1} = (C_{\text{outlet}} / C_{\text{inlet}}) \quad (10)$$

Equating equations 7 and 10

$$\frac{C_{\text{outlet}}}{C_{\text{inlet}}} = \exp \left( - \frac{a K_o x}{v} \right) = e^{-1} \quad (11)$$

Taking the ln of eq. 11 and solving for x for one mass transfer unit,  $N = 1$ , gives  $L_m$

$$\frac{a K_o x}{v} = 1 \quad \text{Solving for x for 1 mass transfer unit:} \quad x = \frac{v}{a K_o} = L_m \quad (12)$$

Equation 12 provides the distance  $L_m$  the gas must travel in the catalyst to reduce the NO concentration by one mass transfer unit ( 63.21 % reduction of NO ).

For catalyst with small tubes, the gas flow is in laminar flow (i.e.  $Re < 2100$  ). In laminar flow, the gas film mass transfer coefficient  $k_m$  is related to the Sherwood Number (which has the magnitude of 4.4 for cylindrical channels) by:

$$Sh = \frac{\text{Total mass transfer}}{\text{molecular mass transfer}} = \frac{k_m D}{\vartheta} \quad (13)$$

Solving for the gas film mass transfer coefficient  $k_m$

$$k_m = \frac{4.4 \vartheta}{D} \quad (14)$$

The surface area  $a$  ( $\text{cm}^2/\text{cm}^3$ ) inside the tube of the honeycomb catalyst is given by

$$a = \frac{L \pi D}{L \pi (D^2 / 4)} = \frac{4}{D} \quad (15)$$

Solving for the tube diameter  $D = 4 / a$  (16)

Some example data ( assuming that  $K_o = k_m$  ) is shown below:

	Holes/sq. inch of catalyst support		
	200	300	400
Open Area (%)	72	65	77
Effective Hole Diameter ( inches )	.059	.046	.044
Gas Vel. in holes (ft/sec)	27.7	30.8	26.0
Reynolds Numbers	153	133	107
Length of 1 Mass Transfer Unit ( inches )	0.80	0.54	0.42
Gas Pressure Drop (" H <sub>2</sub> O )	1.8	2.0	1.5

**Effect of Reaction Kinetics** The reduction reactions shown in equations 1 and 2 are not actually "instantaneous" and hence the effect of the reaction kinetics on the NO reduction should be included. The overall mass transfer coefficient  $K_o$  can be given by:

$$\frac{1}{K_o} = \frac{1}{k_m} + \frac{1}{k_r} \quad (17)$$

where  $k_r$  is the reaction rate constant. In reality, there are a number of reaction rate constants, however, for this example they will be combined into the one reaction rate constant,  $k_r$ . One then can calculate the overall mass transfer coef.  $K_o$  and then use the equation 7 to obtain the concentration ratio  $C/C_o$

$$\frac{C}{C_o} = \exp\left(-\frac{a K_o x}{v}\right) \quad (7)$$

How does one obtain the magnitude of this pseudo reaction rate coefficient  $k_r$  from experimental data? An example calculation is provided below.

### Example Calculation of NO Catalytic Reduction Reaction Rate Constant $k_r$

Given: 200 CPSI cell density,  $T=350^\circ\text{C}$  ( $662^\circ\text{F}$ ), Space vel. =  $20,000 \text{ hr}^{-1}$ ,  $\text{NH}_3/\text{NO} = 0.95/1$

Diffusivity of NO at  $662^\circ\text{F} = 0.8 \text{ cm}^2/\text{sec}$ . Hole Dia. =  $0.059 \text{ "}$  =  $.00492 \text{ ft}$  Cat. L =  $4.5 \text{ ft}$

NOx reduction = 95% for 42 ppm NO at cat. inlet (Fig. 13 or Engelhard paper by Durilla, et al)

Find: Magnitudes of  $k_m$ ,  $k_r$ , and  $K_o$

- Solve for catalyst surface area  $a = (4/D) = (4/.00492\text{ft}) = 813.56 \text{ ft}^2/\text{ft}^3$
- Solve for gas vel.  $v = (\text{Space Vel, hr}^{-1}) (\text{Cat. Length}) = (20,000 \text{ hr}^{-1})(4.5 \text{ ft}) = 25 \text{ ft}/\text{sec}$ .
- Solve for  $K_o$

$$K_o = -\frac{v}{a x} \ln\left(\frac{C}{C_o}\right) = -\frac{(25 \text{ ft}/\text{sec})}{(813.56 \text{ ft}^2/\text{ft}^3)(4.5 \text{ ft})} \ln(0.95) = -(0.006829)(-0.051293) = 0.0003503 \frac{\text{ft}}{\text{sec}}$$

- Solve for  $k_m$  with equation 14

$$k_m = \frac{(4.4 \text{ } \emptyset)}{D} = \frac{(4.4)(0.8 \text{ cm}^2/\text{sec})}{(0.00492 \text{ ft})(30.48 \text{ cm}/\text{ft})} = 23.473 \frac{\text{cm}}{\text{sec}} = 0.7701 \frac{\text{ft}}{\text{sec}}$$

- Solve for  $k_r$  with equation 17

$$\frac{1}{k_r} = \frac{1}{K_o} - \frac{1}{k_m} = \frac{1}{0.0003503 \text{ ft}/\text{sec}} - \frac{1}{0.7701 \text{ ft}/\text{sec}} = 2,854.7 - 1.2985 = 2,853.40 \text{ sec}/\text{ft}$$

$$k_r = 0.0003505 \text{ ft}/\text{sec} = 0.010682 \text{ cm}/\text{sec}$$

### Gas Pressure Drop Across the Catalyst

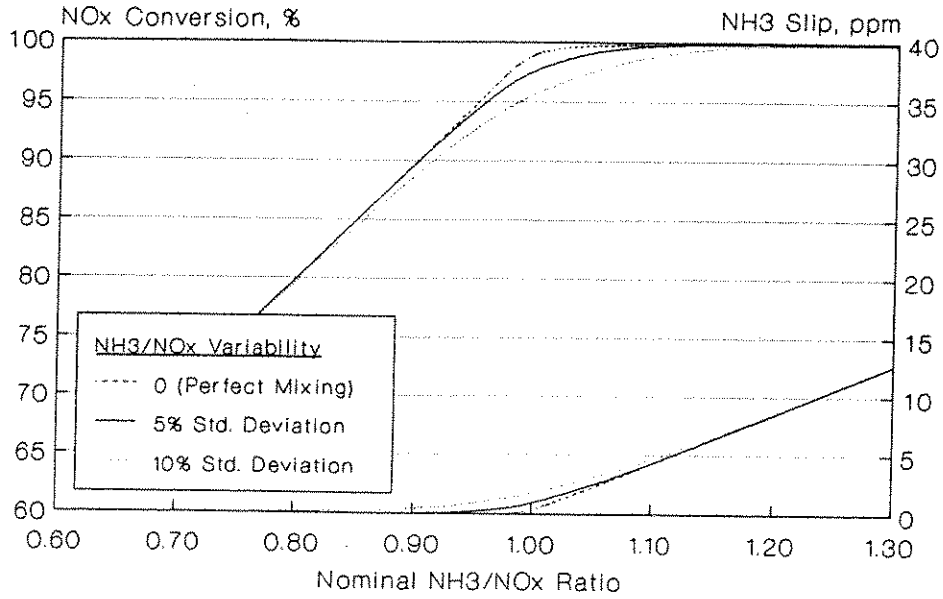
The gas pressure drop across the catalyst can be calculated by  $\Delta p = \frac{2 f L v^2 \rho}{g_c D}$

The Fanning friction factor  $f$  is  $16/\text{Re}$  for circular tubes and  $14/\text{Re}$  for square channels.

The other variables are  $L$  = total length of catalyst tube,  $v$  the gas velocity,  $\rho$  the fluid gas density,  $g_c$  the gravitational constant, and  $D$  the effective diameter of the channel or tube.

Figure 13:

### Gas Turbine Installations Are Relatively Insensitive To Incomplete NH<sub>3</sub>/NO<sub>x</sub> Mixing



20,000 1/hr VHSV, 42 ppm NO<sub>x</sub>, 350 deg C

Figure 14:

### Composite SCR Catalyst Aging Correlation In Commercial Service

