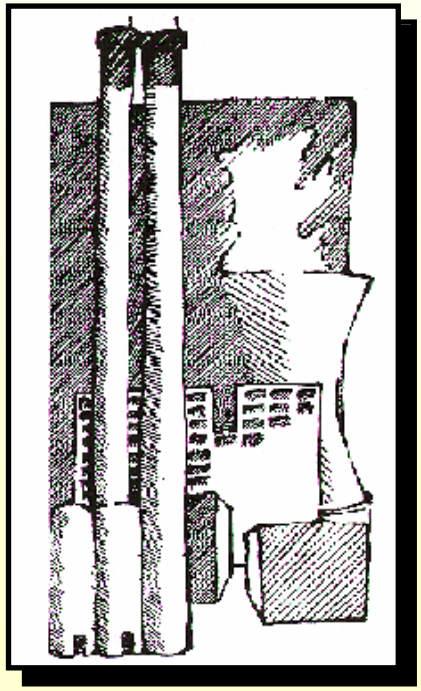
SULFURIC ACID EMISSIONS FROM COAL-FIRED BOILERS



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Nenad Sarunac

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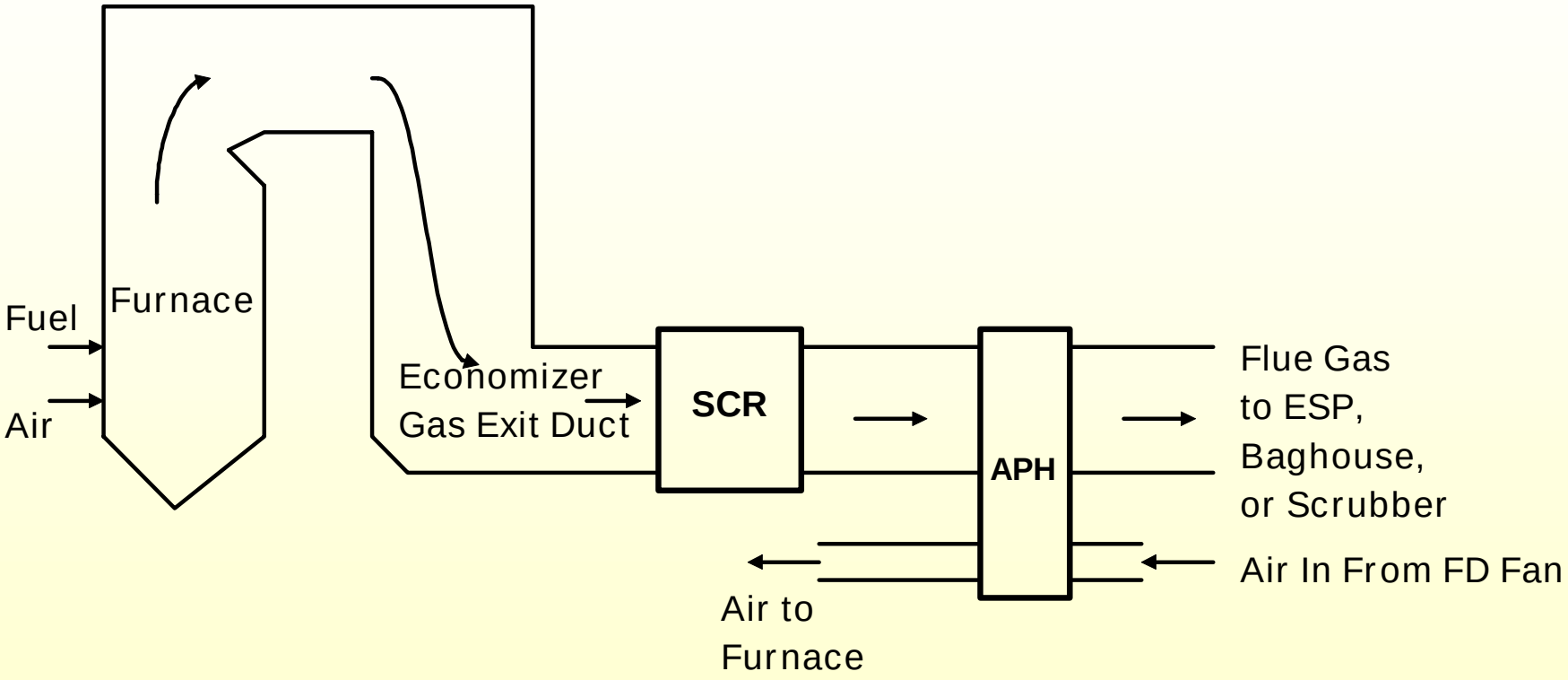
Bethlehem, PA 18015

STACK EMISSIONS OF H_2SO_4

- Depend on:
  - Fuel Sulfur
  - Boiler Design
  - SCR Design
  - Boiler and SCR Operating Conditions
- Site Specific

FORMATION OF SO_3



KEY PROCESSES

- SO_3 Formed in Boiler and SCR
- Converted to H_2SO_4 in Air Preheater
- Some Condenses in Air Preheater
- Some Deposited Onto Fly Ash
- Remainder Flows Out Stack as Mixture of H_2SO_4 Vapor and Liquid Droplets

PRESENTATION OUTLINE

- SO_3 Formation Mechanisms
- Acid Condensation and Evaporation in Air Preheater Flow Passages
- Acid Adsorption and Condensation on Particles
- Stack Emissions

Boiler and SCR design and operating conditions and fuel properties affect quantity of SO_3 produced

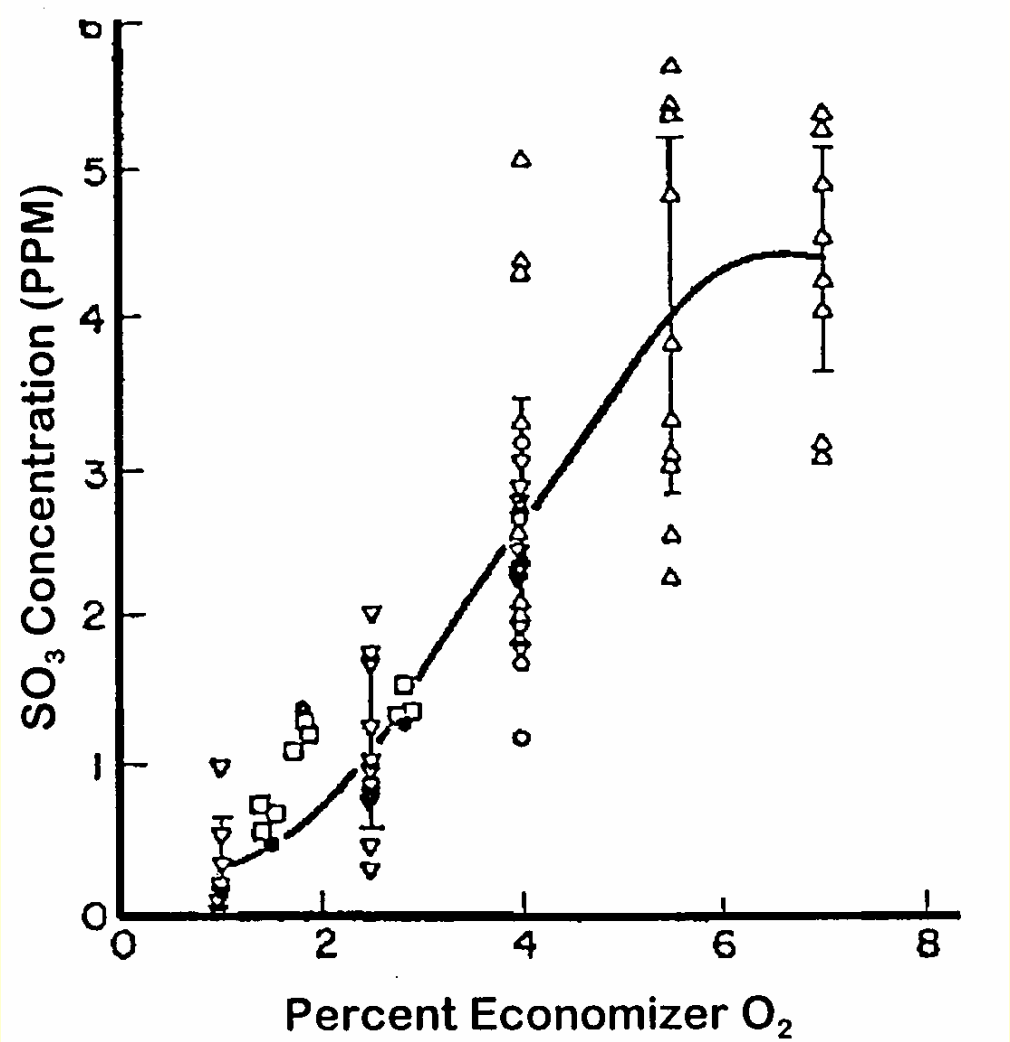
- Fuel Sulfur Content and Ash Composition
- Excess O_2 Level
- Gas Temperature and Residence Time Distribution in Boiler and SCR
- Tube Material and Surface Area
- Very Site Specific

SO_3 FORMATION WITHOUT SCR

Measured SO_3 Concentrations in Economizer Gas Exit Ducts of Three Coal-Fired Boilers

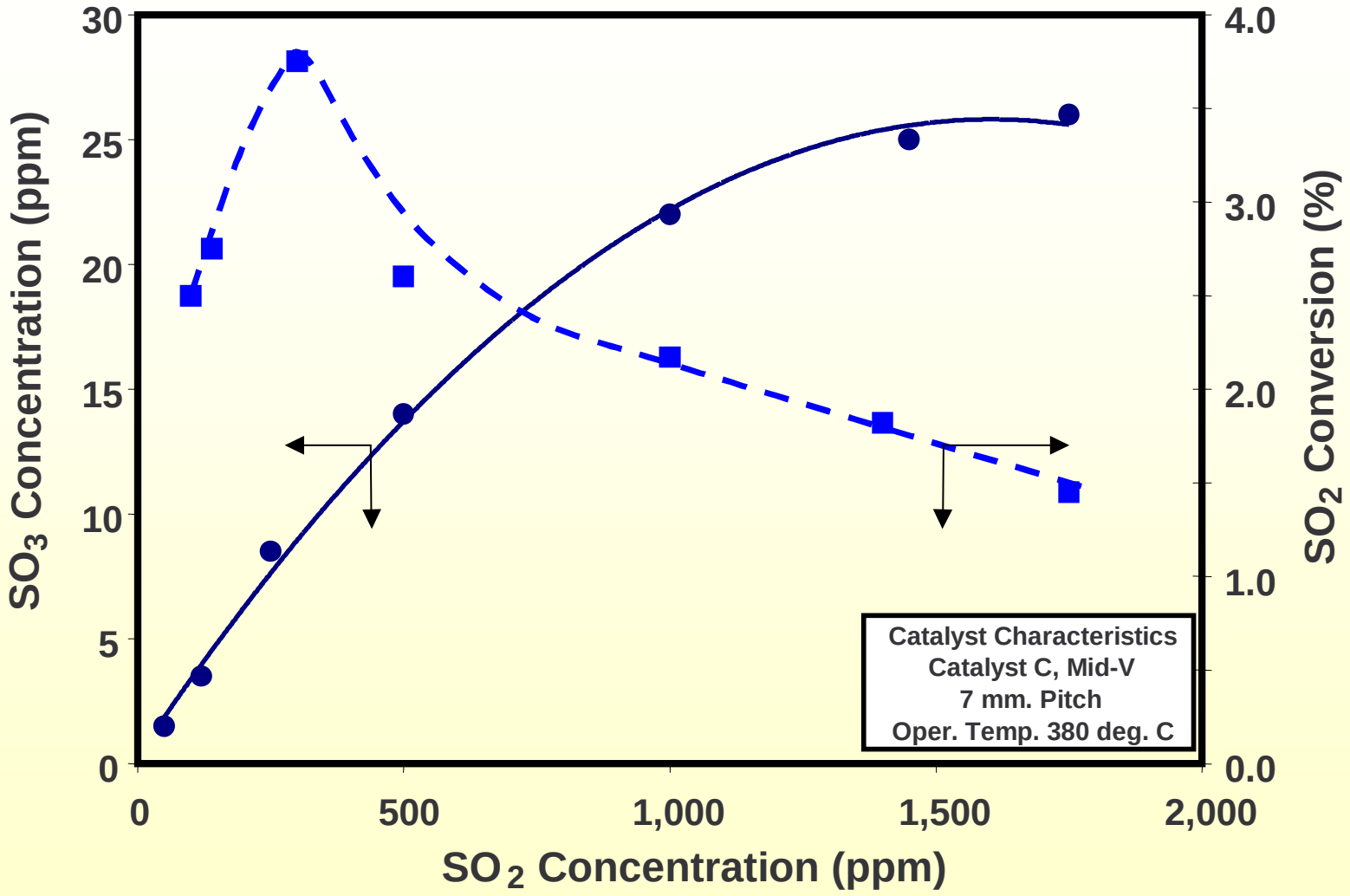
Pulverized Coal-Fired; 2 – 3% Sulfur Coal			
Unit	SO_3 (ppm)	Unit Load (MW)	O_2 (%) at Economizer Gas Exit
A	1 to 2.5	585	2 to 4
A	2.5 to 5	425 & 300	4 to 7
B	20	640	--
C	21 to 24	700	4 to 5
C	27	180	10

SO_3 FORMATION WITHOUT SCR



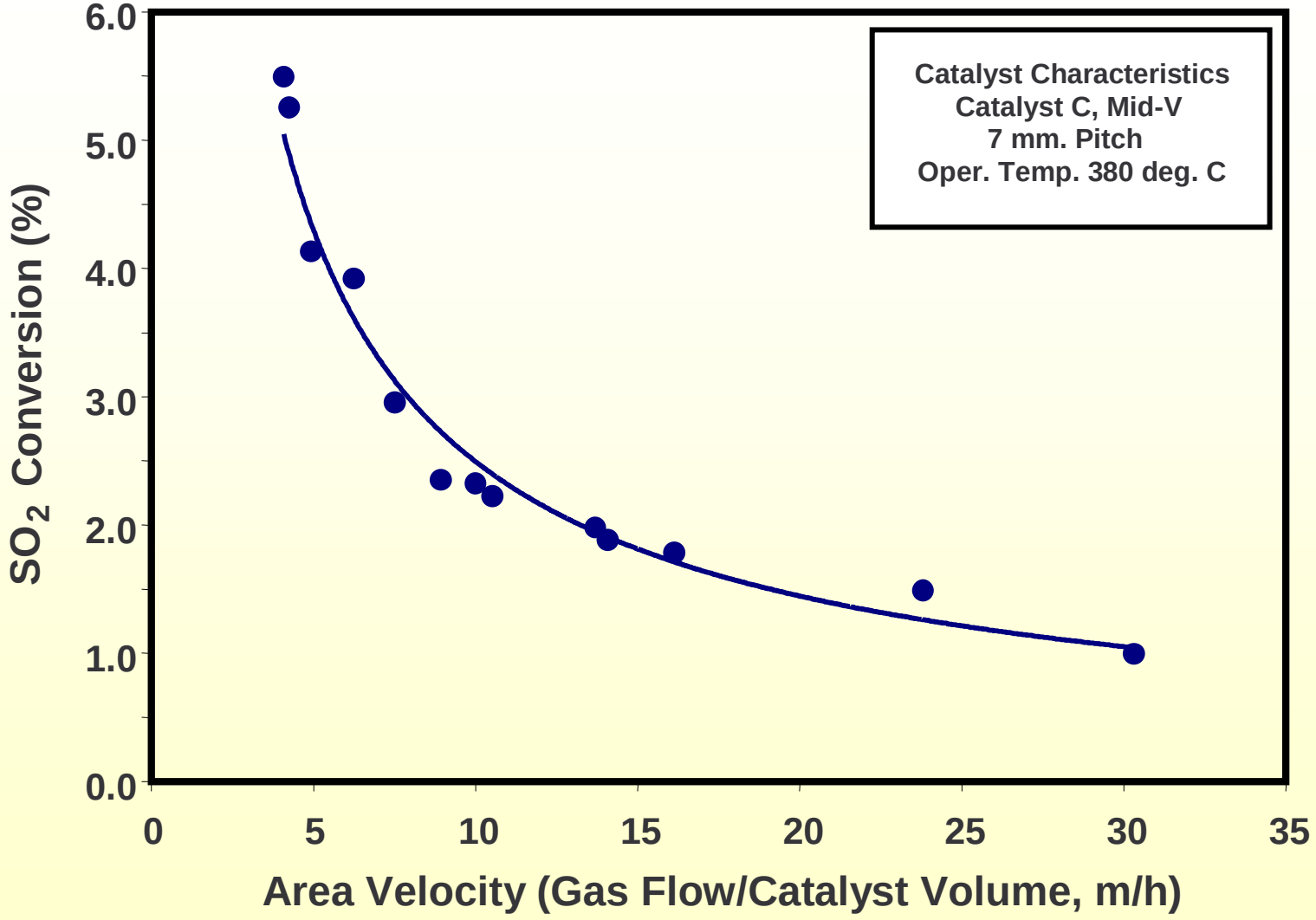
CONTRIBUTION OF SCR

Effect of SO_2 Concentration on the Oxidation of SO_2 to SO_3



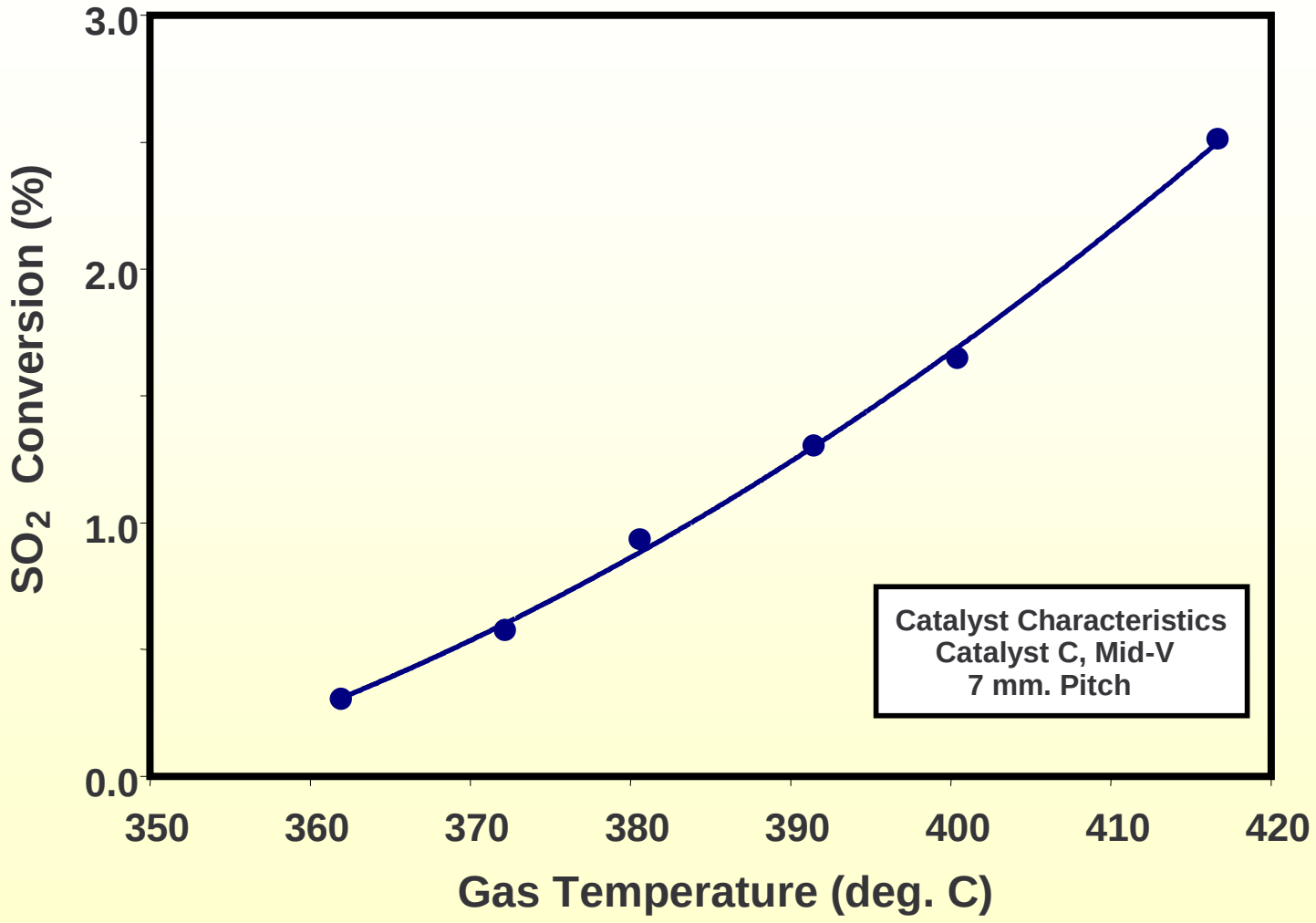
Ref. Svachula, J., et al., Ind. Eng. Chem. Res. 1993, 32, 826-834

Effect of Area Velocity on the Oxidation of SO_2 to SO_3



Ref. Svachula, J., et al., Ind. Eng. Chem. Res. 1993, 32, 826-834

Effect of Gas Temperature on the Oxidation of SO_2 to SO_3



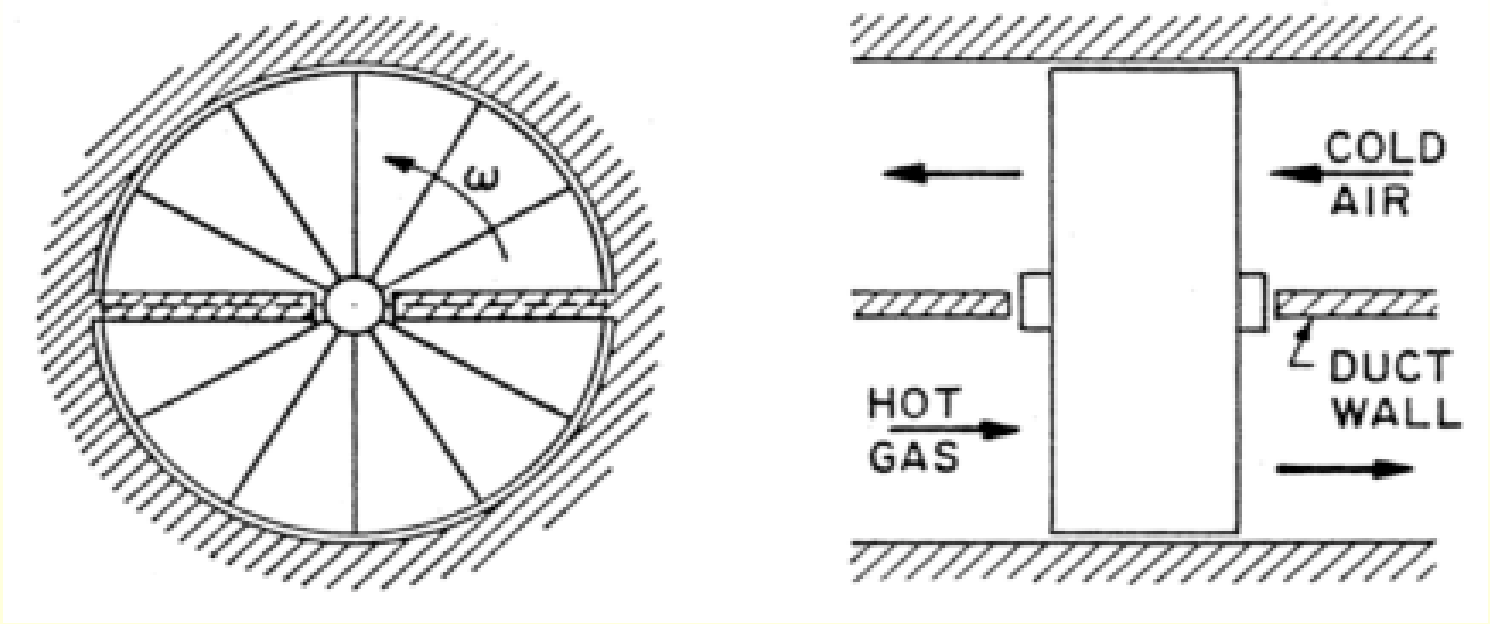
Ref. Svachula, J., et al., Ind. Eng. Chem. Res. 1993, 32, 826-834

EFFECT OF VANADIUM LOADING ON SO_2 OXIDATION (REACTION TEMPERATURE = 360°C)

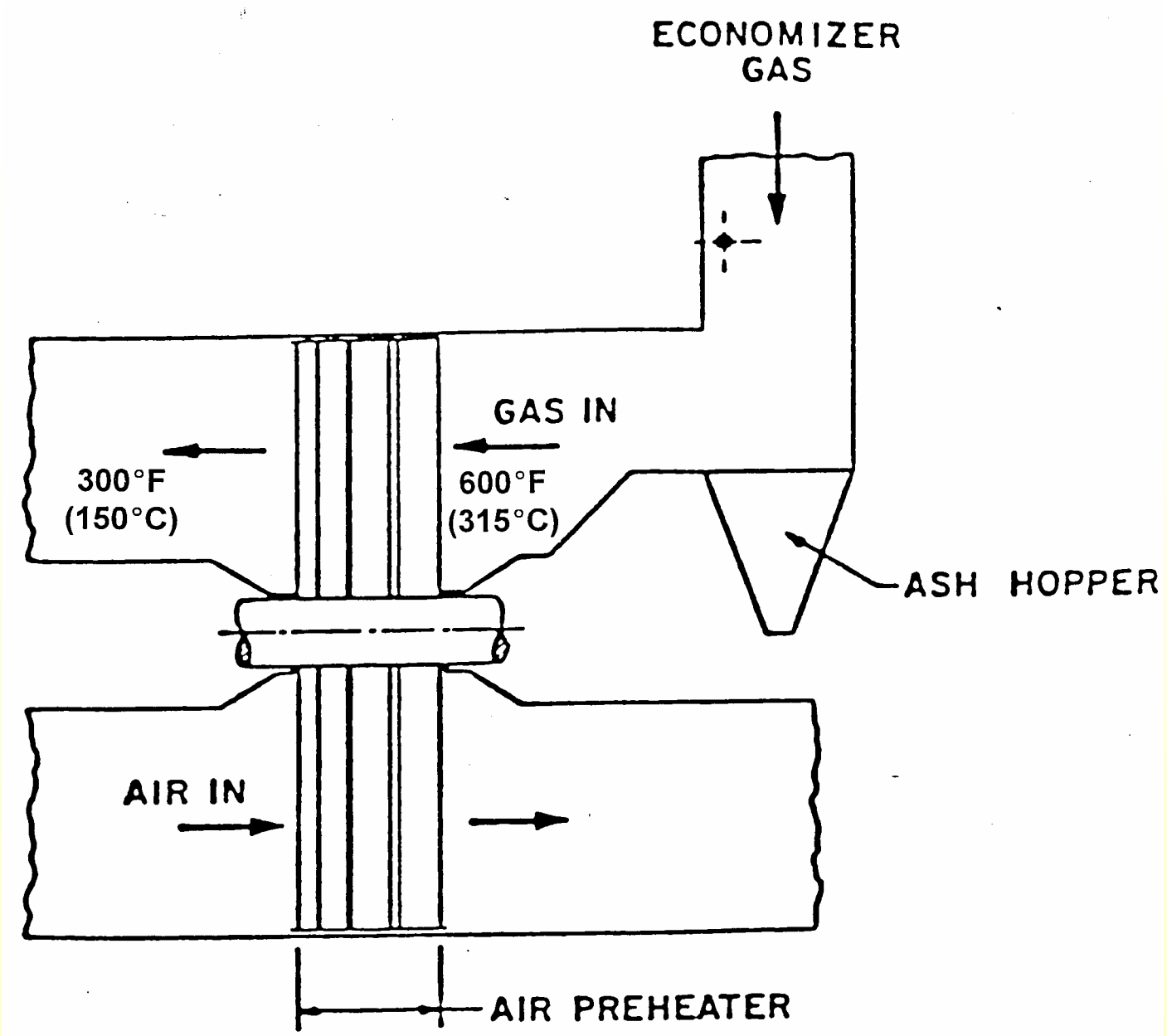
CATALYST	V LOADING	CONVERSION (%)
D	Low	0.2
A	Medium	1.4
E	High	6.3

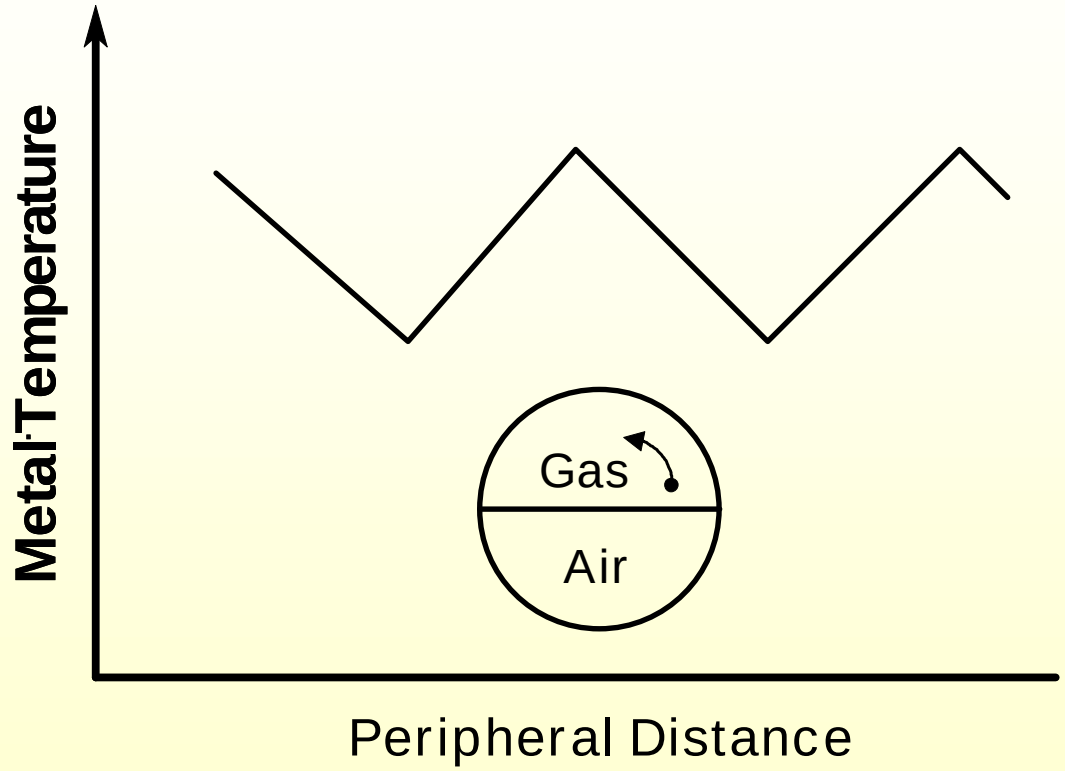
Ref. Svachula, J., et. al, Ind. Eng. Chem. Res. 1993, 32, 826-834

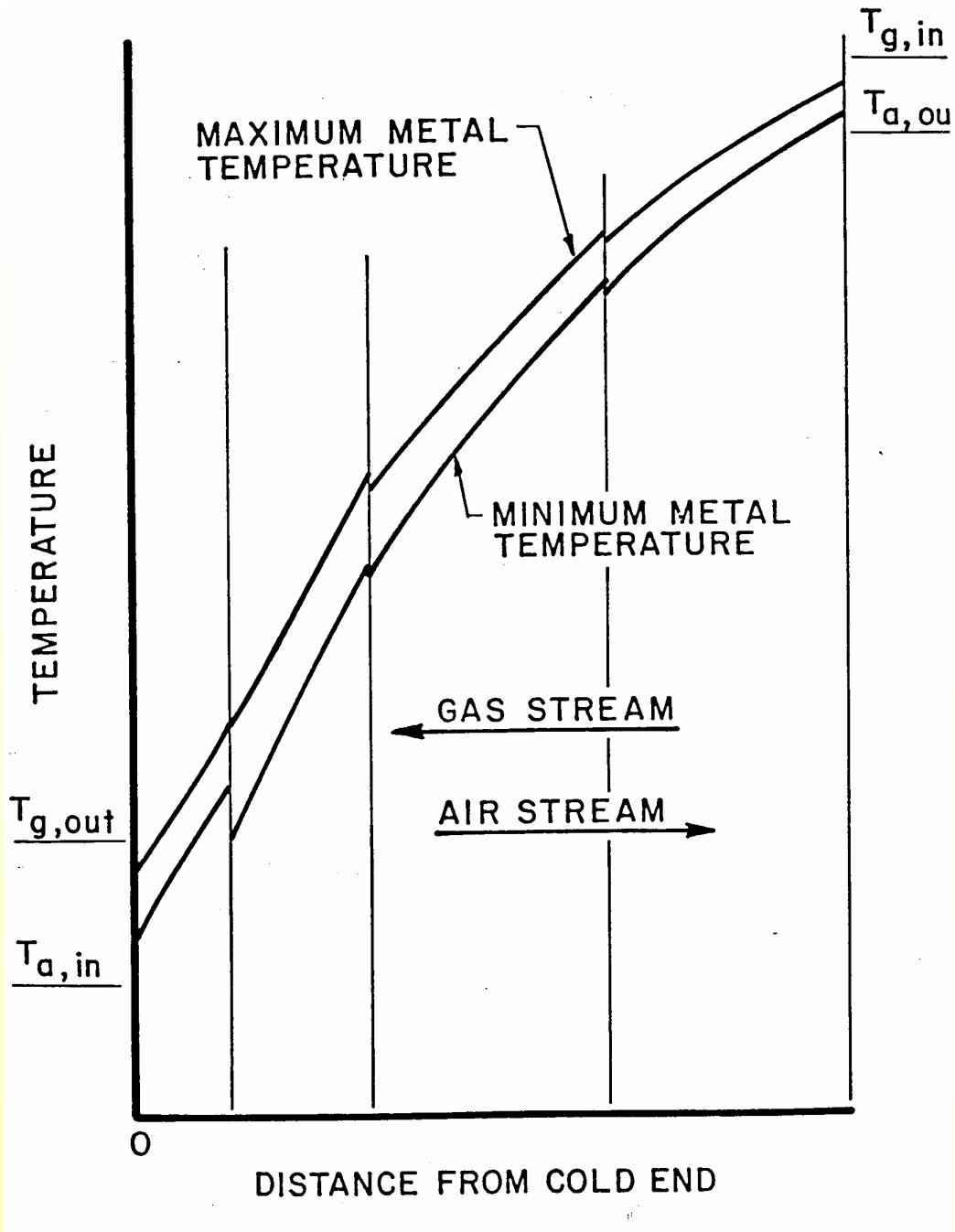
BACKEND PROCESSES

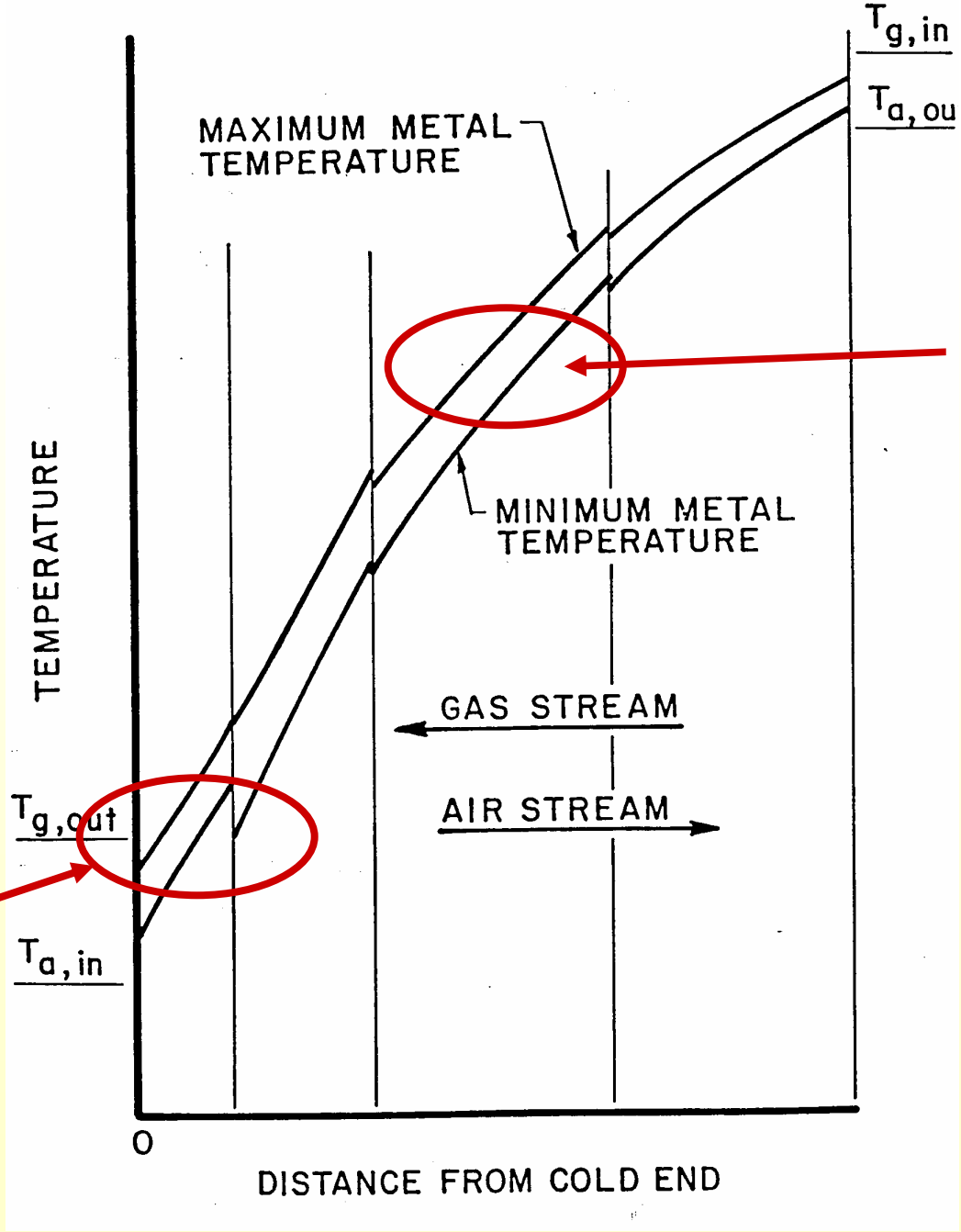


The rotating regenerative air preheater transfers heat from hot flue gas to cool incoming air by way of a rotating metal matrix.


ECONOMIZER
GAS
GAS IN
300°F
(150°C)
600°F
(315°C)
ASH HOPPER
AIR IN
AIR PREHEATER

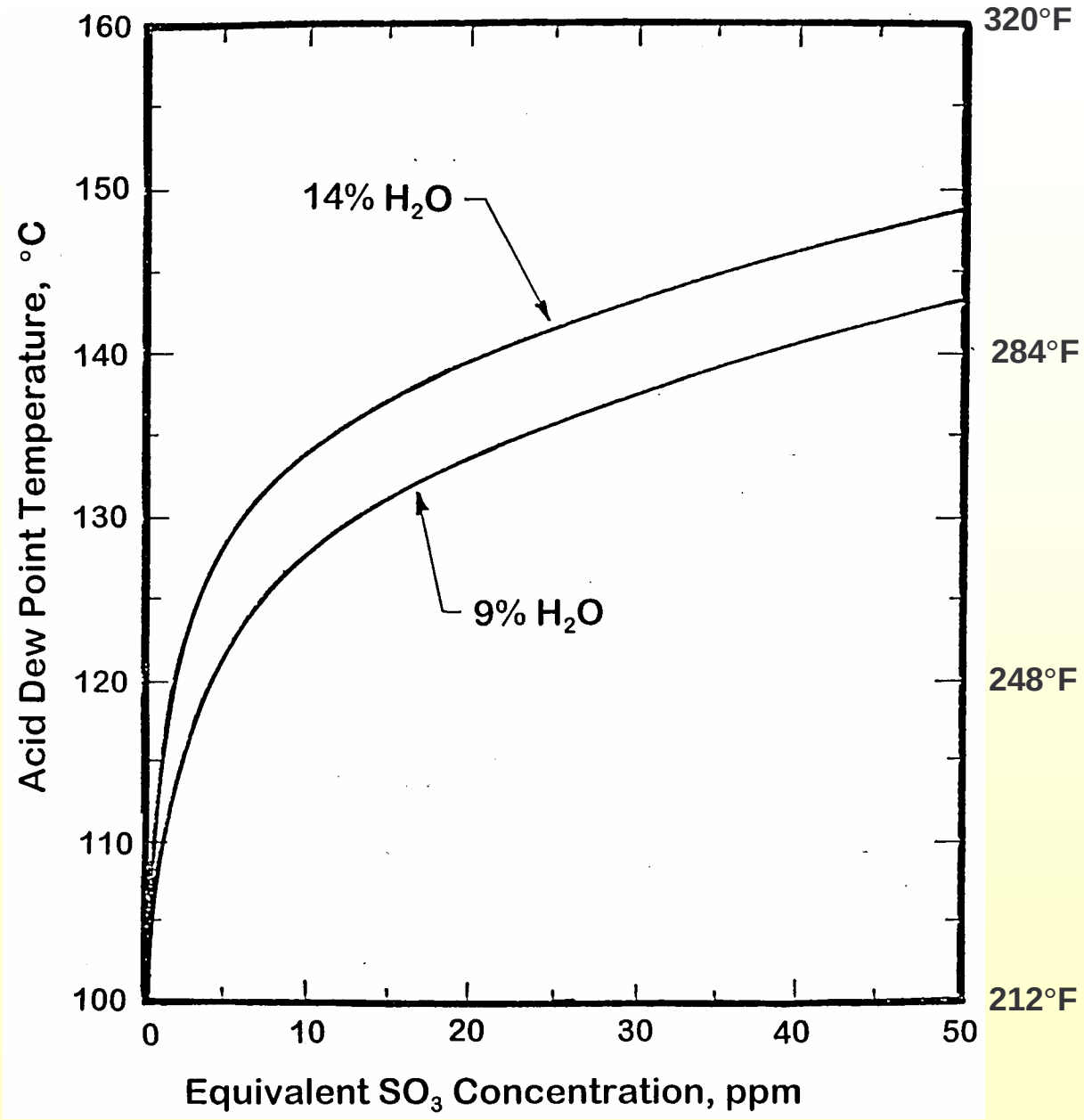

Metal Temperature
Gas
Air
Peripheral Distance

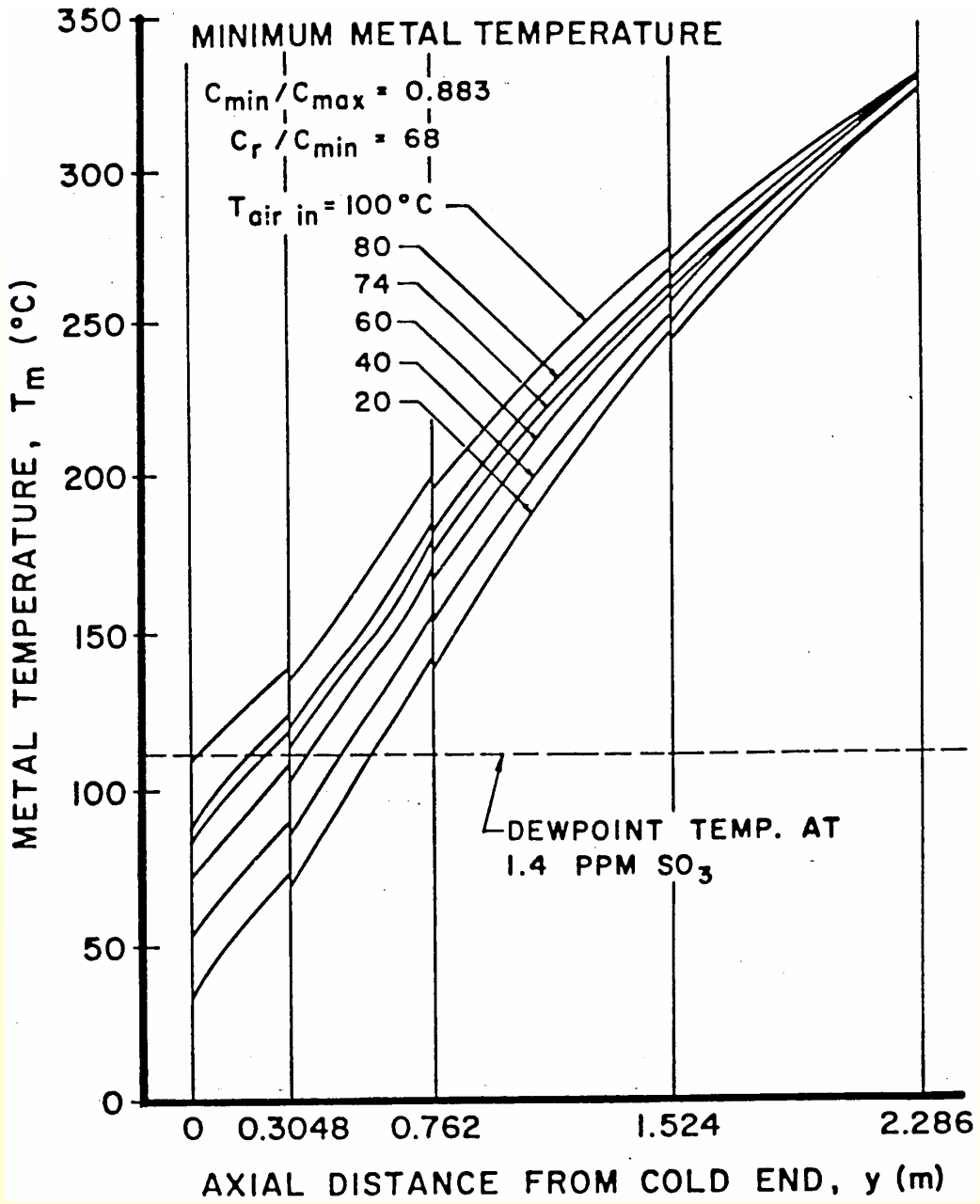

$T_{g,in}$
$T_{a,ou}$
MAXIMUM METAL TEMPERATURE
MINIMUM METAL TEMPERATURE
TEMPERATURE
GAS STREAM
AIR STREAM
$T_{g,out}$
$T_{a,in}$
0
DISTANCE FROM COLD END



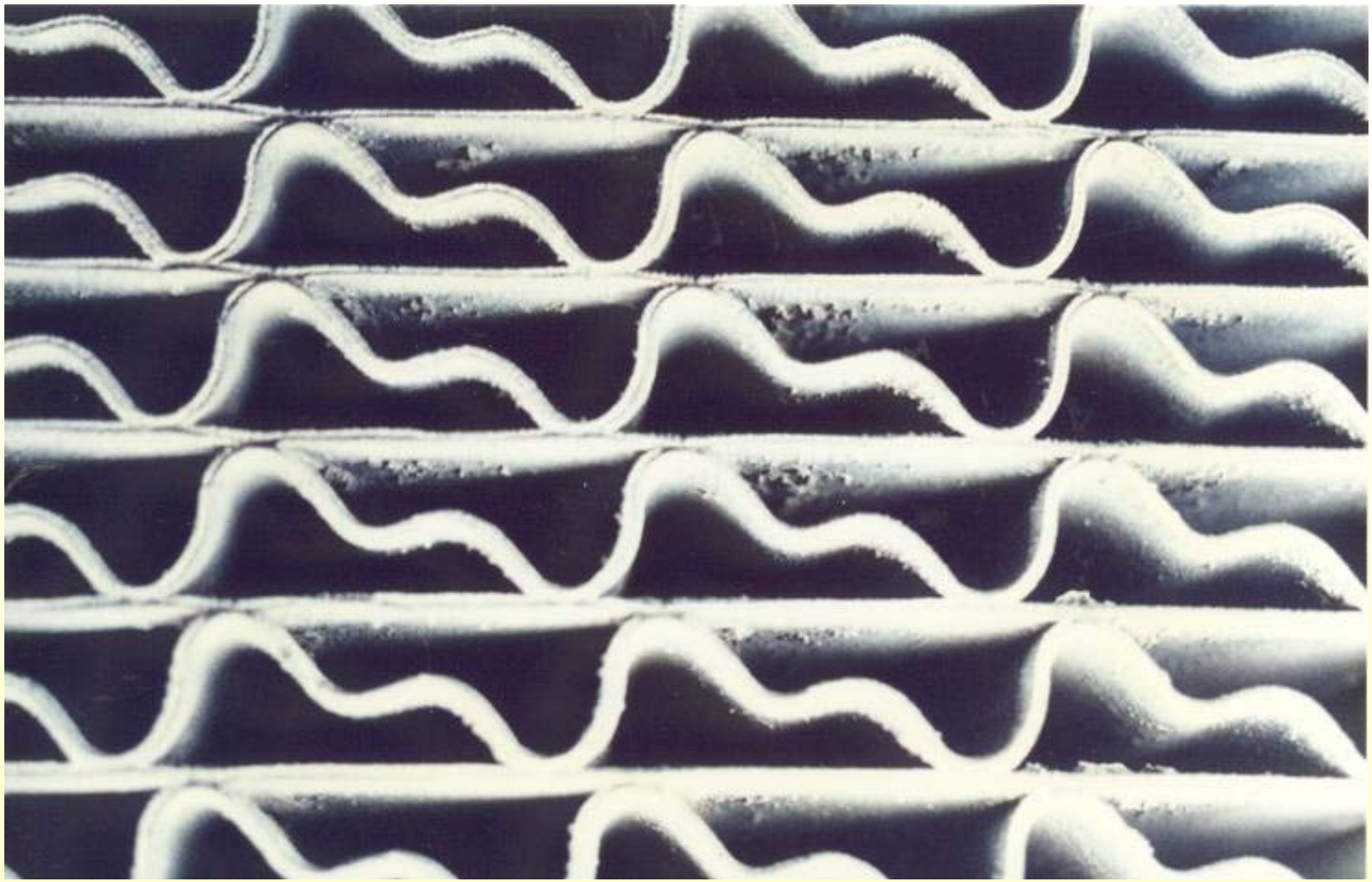
Ammonium Bisulfate Deposition

Sulfuric Acid Deposition

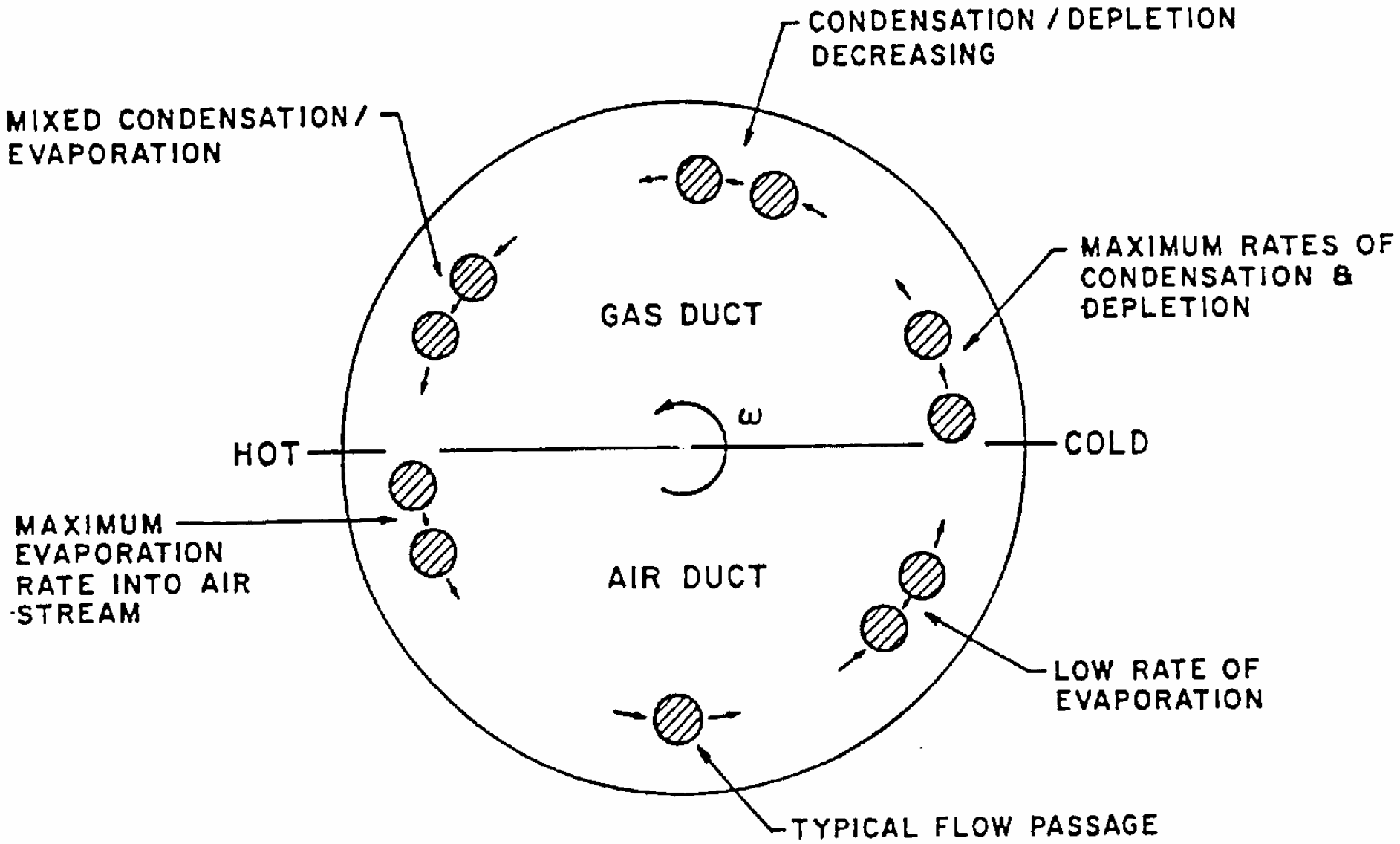

160
150
140
130
120
110
100
320°F
284°F
248°F
212°F
14% H_2O
9% H_2O
Acid Dew Point Temperature, °C
0
10
20
30
40
50
Equivalent SO_3 Concentration, ppm


MINIMUM METAL TEMPERATURE
C_{min}/C_{max} = 0.883
C_r/C_{min} = 68
$T_{air\ in}$ = 100°C
80
74
60
40
20
DEWPOINT TEMP. AT
1.4 PPM SO_3
METAL TEMPERATURE, T_m (°C)
350
300
250
200
150
100
50
0
0
0.3048
0.762
1.524
2.286
AXIAL DISTANCE FROM COLD END, y (m)

CONDENSATION AND EVAPORATION FROM APH BASKET SURFACE



Both Acid Condensation and Evaporation Are Important

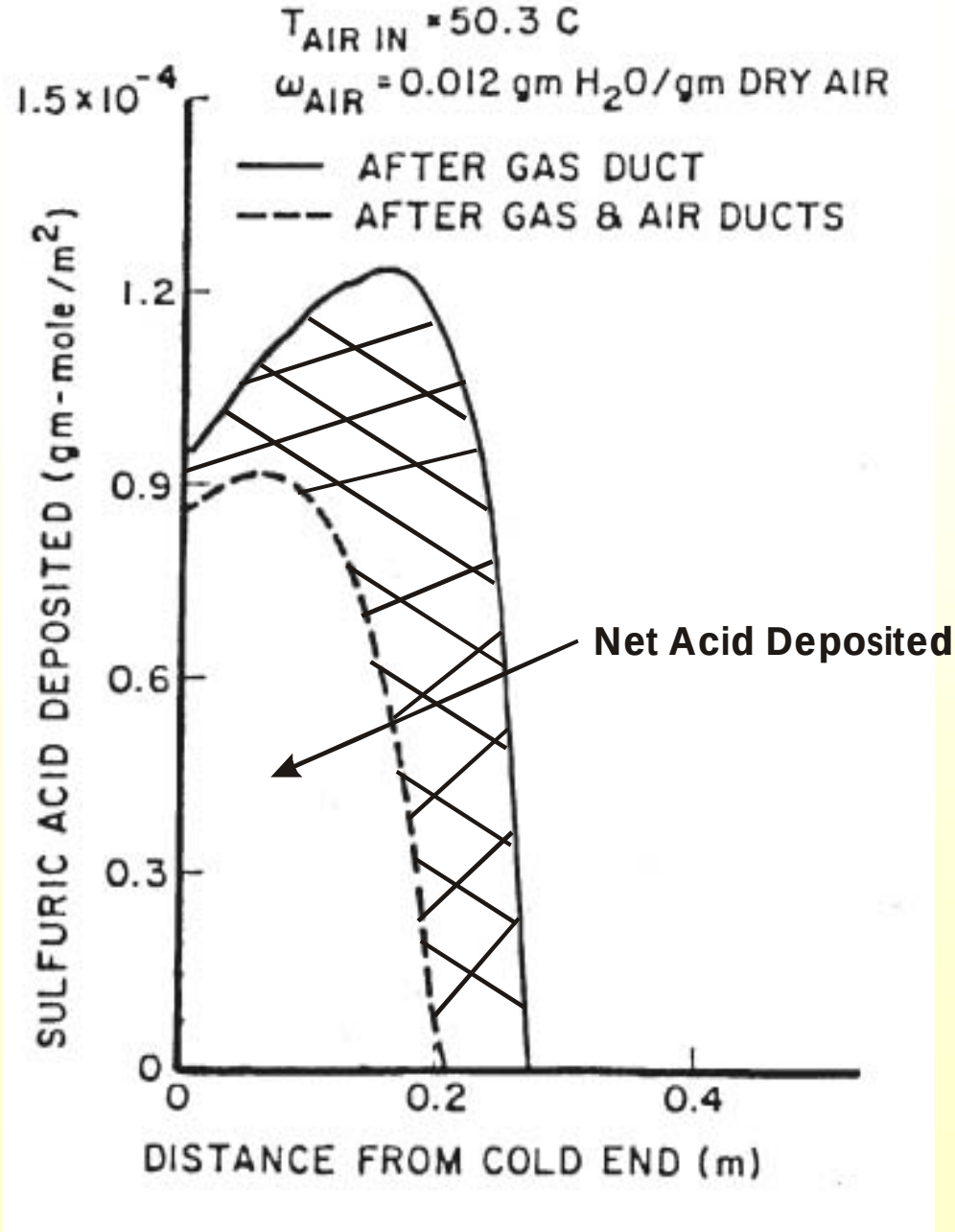


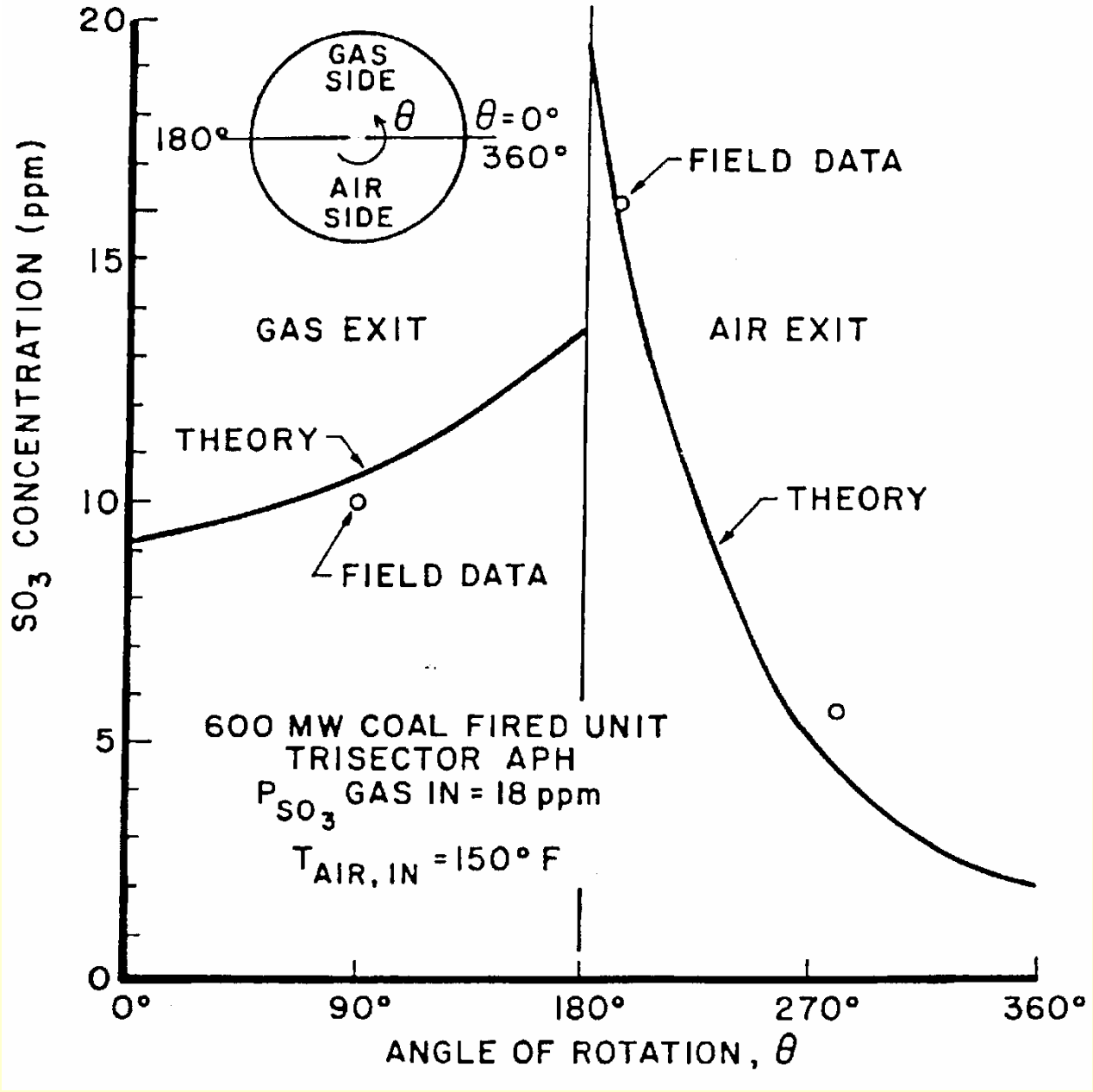
Schematic Representation of APH Acid Deposition Processes

COMPUTATIONAL RESULTS OF RPHSO$_3$ CODE

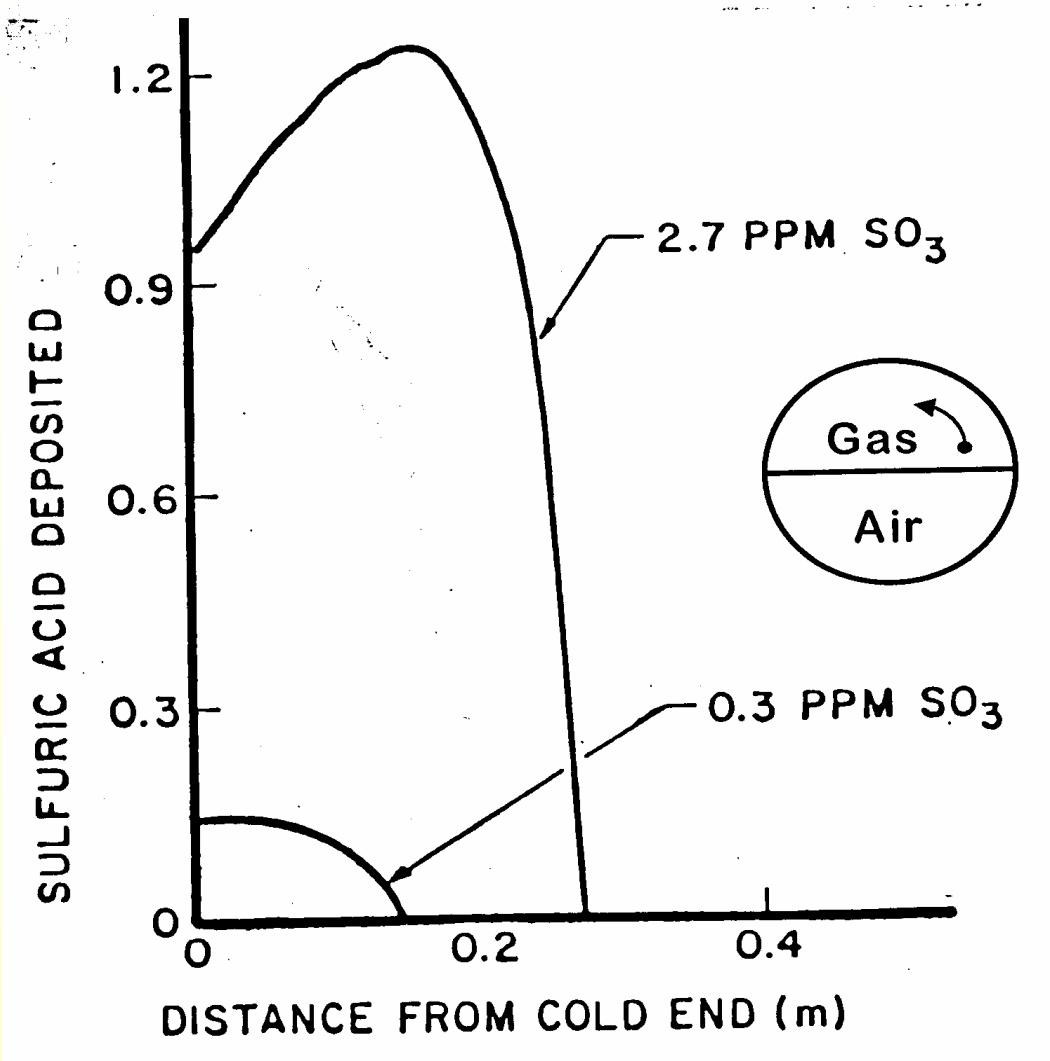
Effect of Flue Gas SO$_3$ Concentration

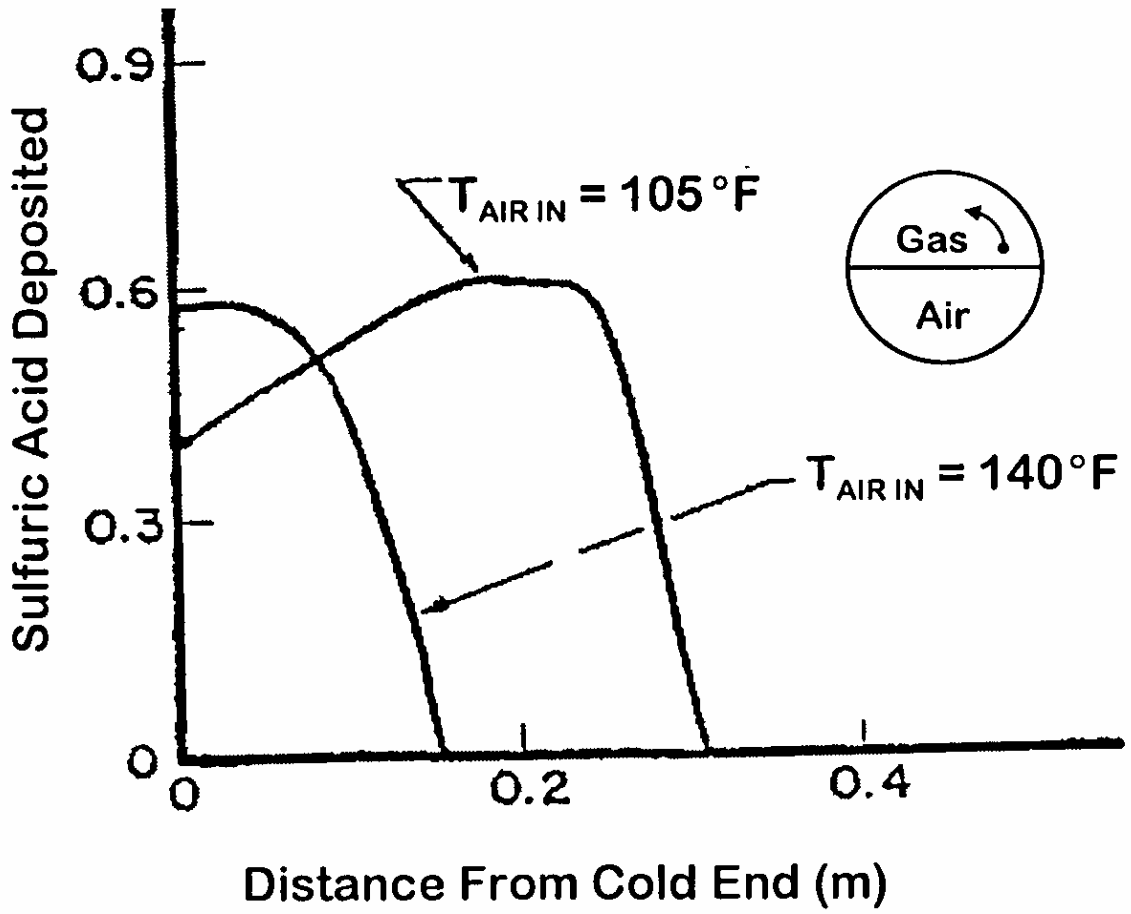
- Peak acid deposition rate is roughly proportional to SO$_3$ concentration.
- Acid dew point increases with SO$_3$ concentration, increasing depth of acid penetration into the cold end basket matrix.


$T_{AIR\ IN}$ = 50.3 C
ω_{AIR} = 0.012 gm H_2O/gm DRY AIR
1.5×10^{-4}
AFTER GAS DUCT
AFTER GAS & AIR DUCTS
SULFURIC ACID DEPOSITED (gm-mole/m^2)
1.2
0.9
0.6
0.3
0
0
0.2
0.4
DISTANCE FROM COLD END (m)
Net Acid Deposited



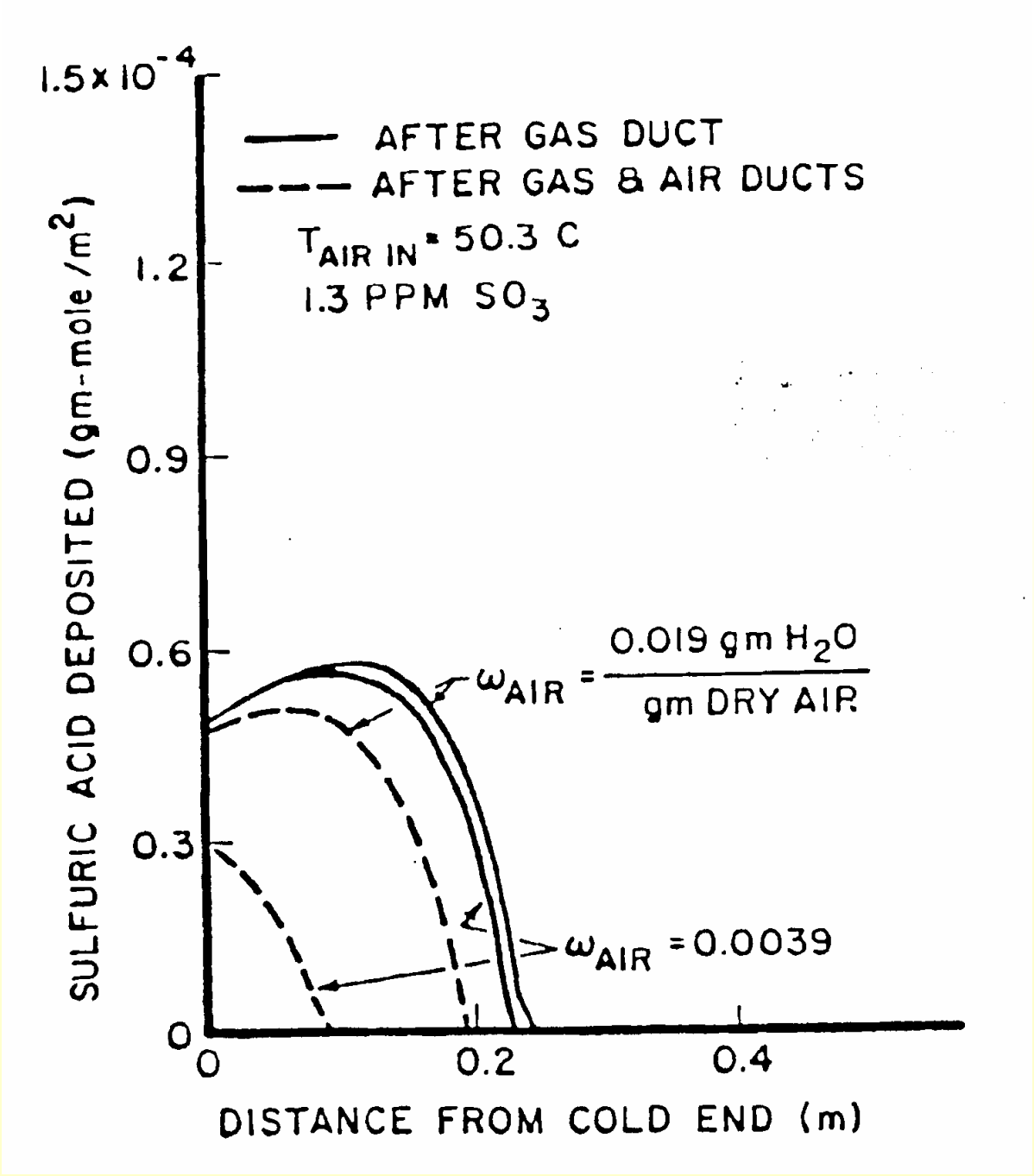
Field Measurements of APH Acid Evaporation and Depletion


1.2
0.9
0.6
0.3
0
SULFURIC ACID DEPOSITED
2.7 PPM SO_3
0.3 PPM SO_3
Gas
Air
0
0.2
0.4
DISTANCE FROM COLD END (m)


Sulfuric Acid Deposited
0.9
0.6
0.3
0
0
0.2
0.4
$T_{AIR\ IN}$ = 105 °F
$T_{AIR\ IN}$ = 140 °F
Gas
Air
Distance From Cold End (m)

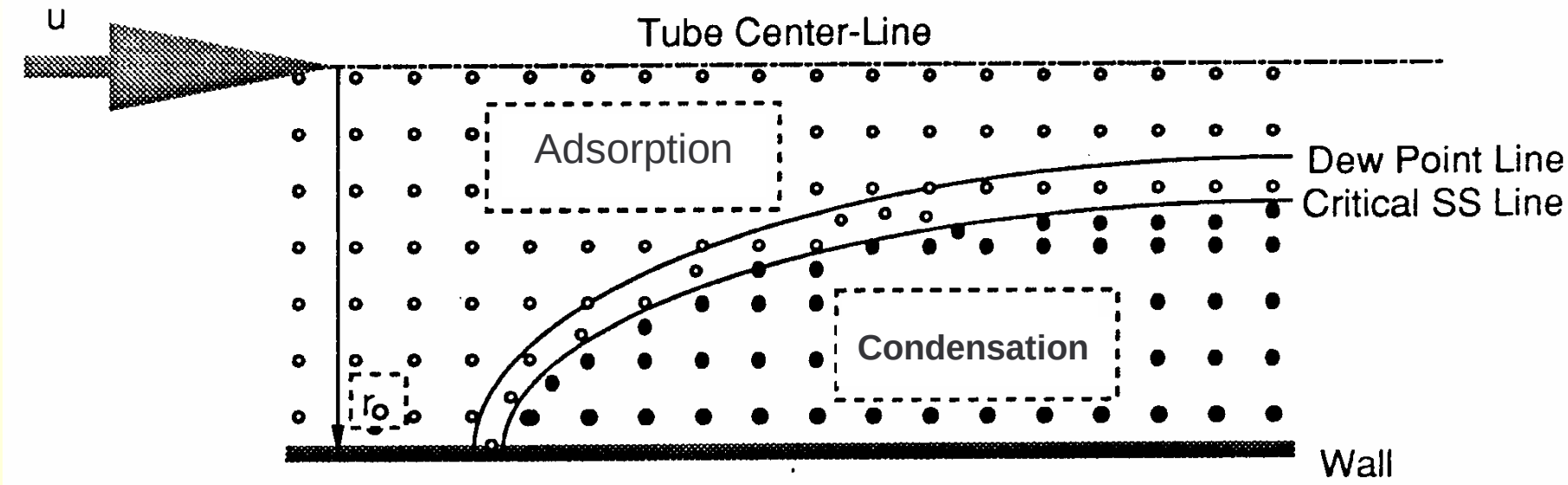
Effect of Inlet Air Moisture

- Dry air has greater ability to evaporate acid from the APH surface.
- The effect of air moisture content on acid condensation is negligible.
- Moisture effect implies that net acid deposition is greater in the summer (moist air) than in the winter (dry air).


1.5 x 10^-4
1.2
0.9
0.6
0.3
0
0
0.2
0.4
AFTER GAS DUCT
AFTER GAS & AIR DUCTS
T AIR IN = 50.3 C
1.3 PPM SO3
ωAIR = 0.019 gm H2O / gm DRY AIR
ωAIR = 0.0039
SULFURIC ACID DEPOSITED (gm-mole/m2)
DISTANCE FROM COLD END (m)

ACID DEPOSITION ONTO FLY ASH

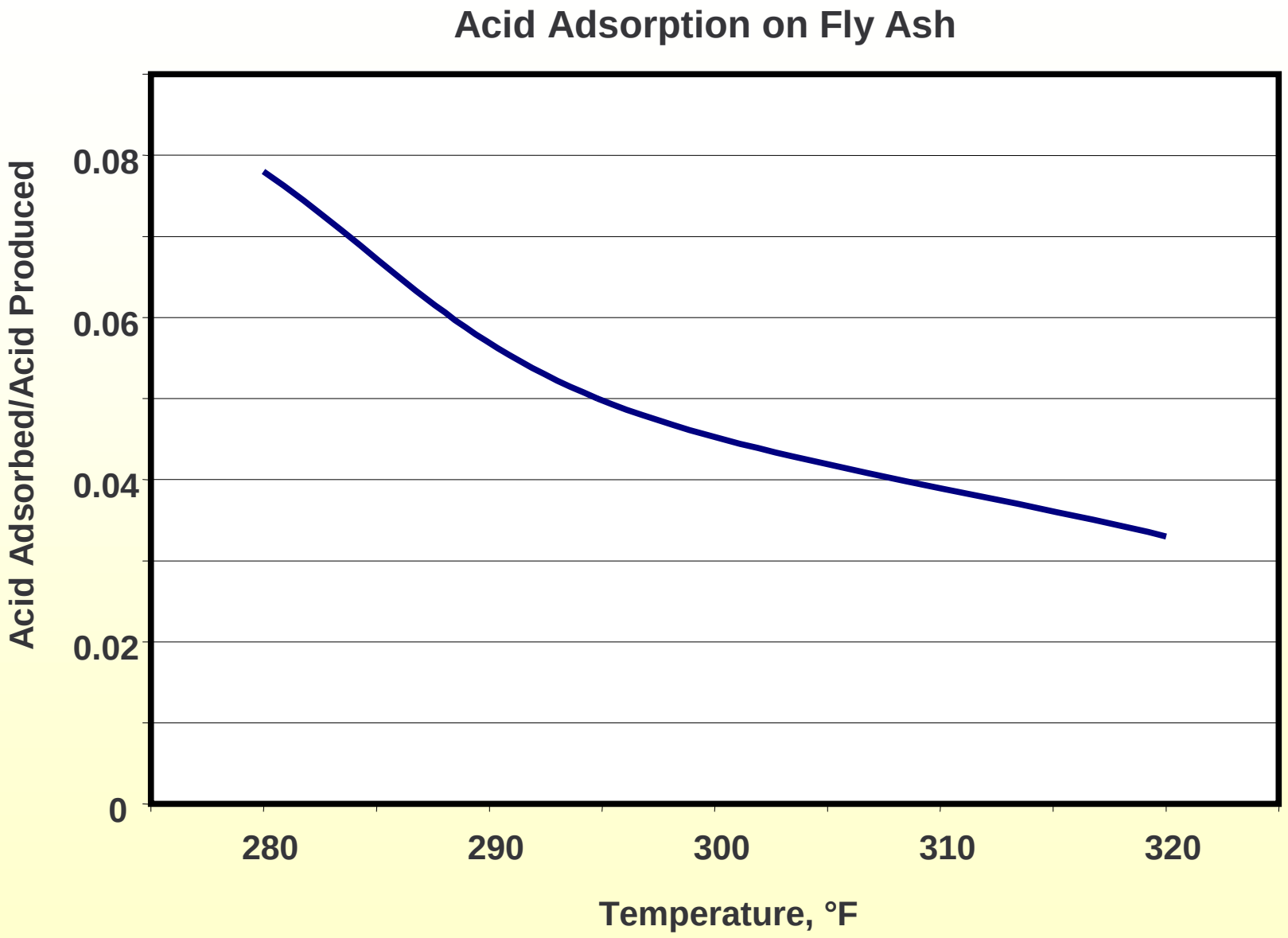
- Adsorption (Occurs Above Dewpoint)
- Condensation

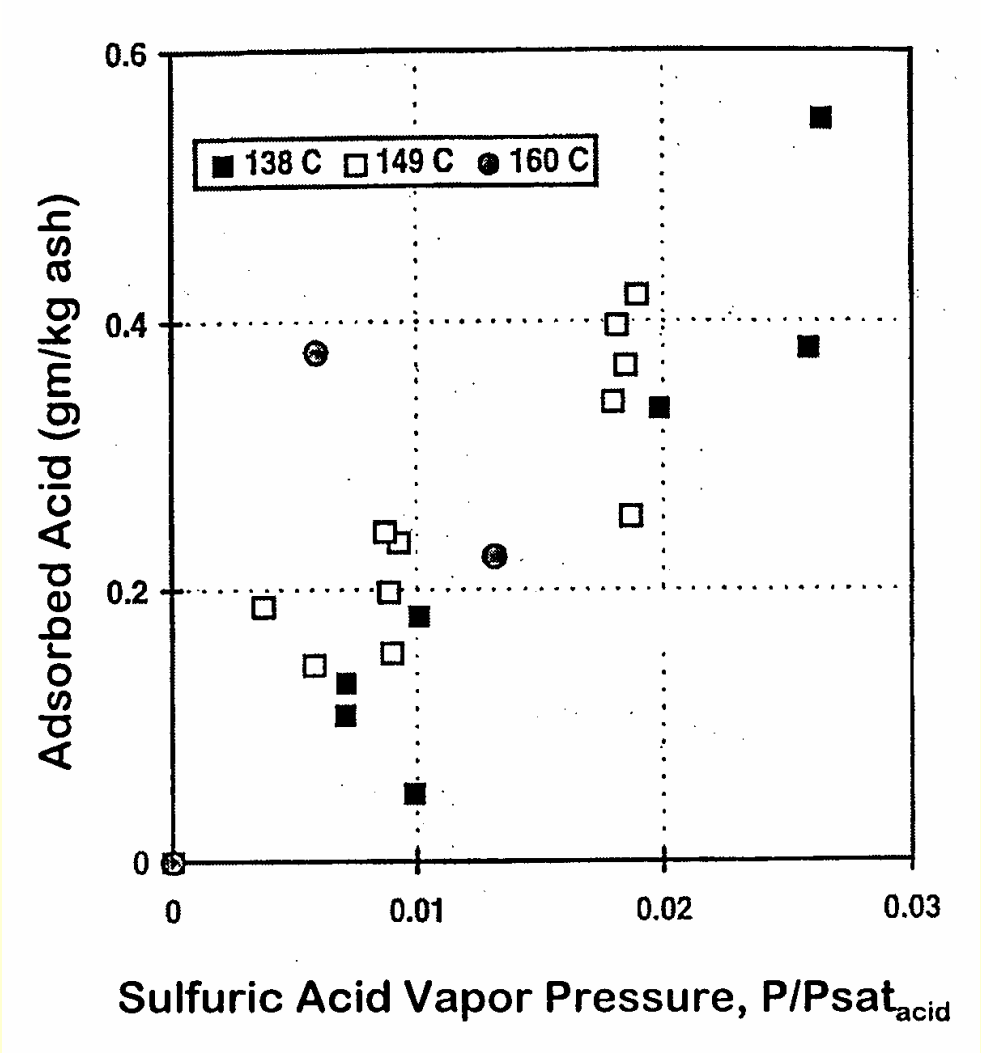


Condensation of Acid and Water Vapor on Particles

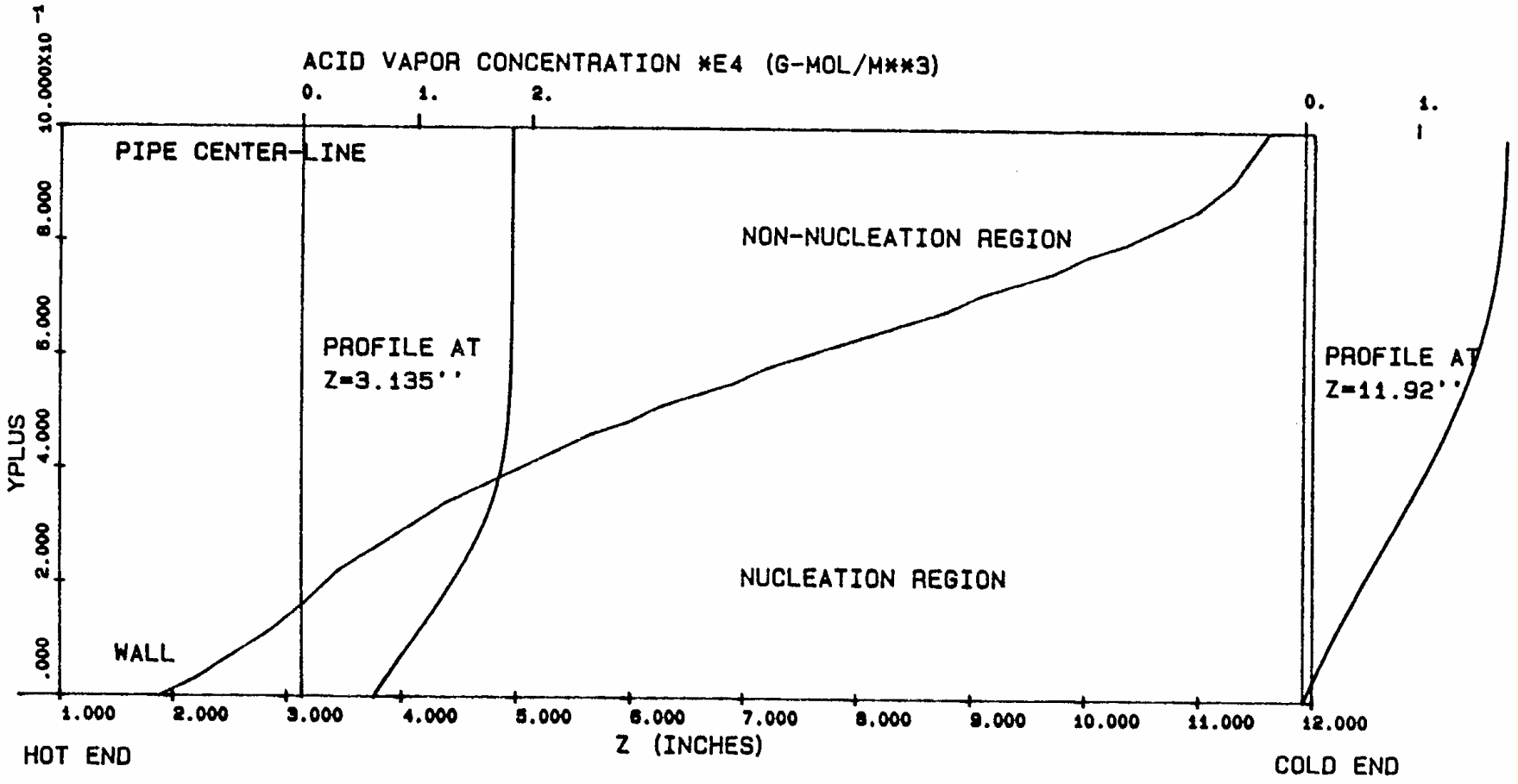
ACID ADSORPTION

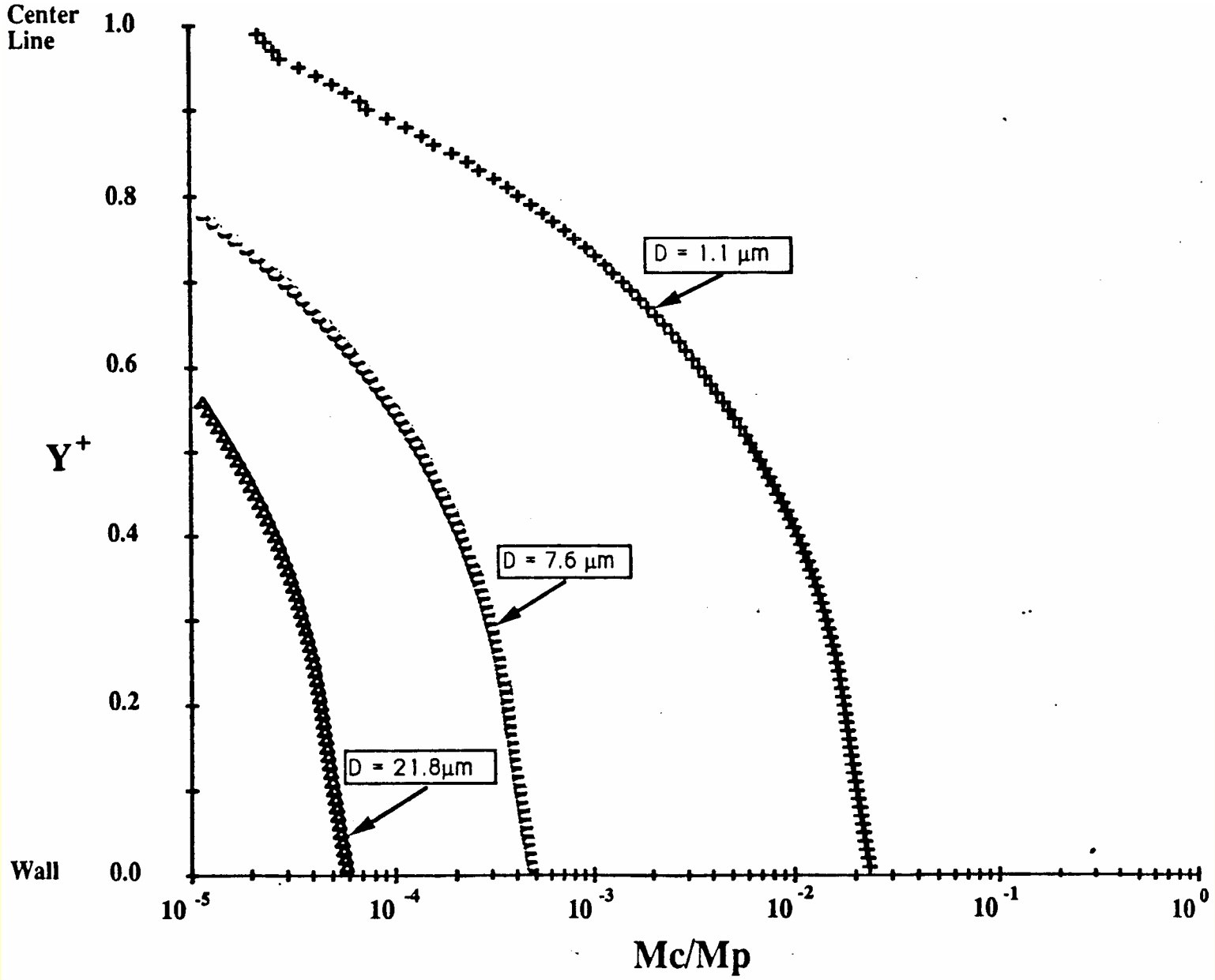
- Laboratory Experiments
- Fly Ash From Pulverized Bituminous Coal
- Amount of Adsorbed Acid Depends on Acid Concentration and Temperature


Acid Adsorption on Fly Ash
Acid Adsorbed/Acid Produced
0.08
0.06
0.04
0.02
0
280
290
300
310
320
Temperature, °F


0.6
0.4
0.2
0
138 C
149 C
160 C
Adsorbed Acid (gm/kg ash)
0
0.01
0.02
0.03
Sulfuric Acid Vapor Pressure, P/Psat$_{acid}$

CONDENSATION ONTO ASH


ACID VAPOR CONCENTRATION *E4 (G-MOL/M**3)
0.
1.
2.
0.
1.
PIPE CENTER-LINE
NON-NUCLEATION REGION
PROFILE AT
Z=3.135''
PROFILE AT
Z=11.92''
NUCLEATION REGION
WALL
YPLUS
10.000X10 -1
8.000
6.000
4.000
2.000
.000
1.000
2.000
3.000
4.000
5.000
6.000
7.000
8.000
9.000
10.000
11.000
12.000
Z (INCHES)
HOT END
COLD END

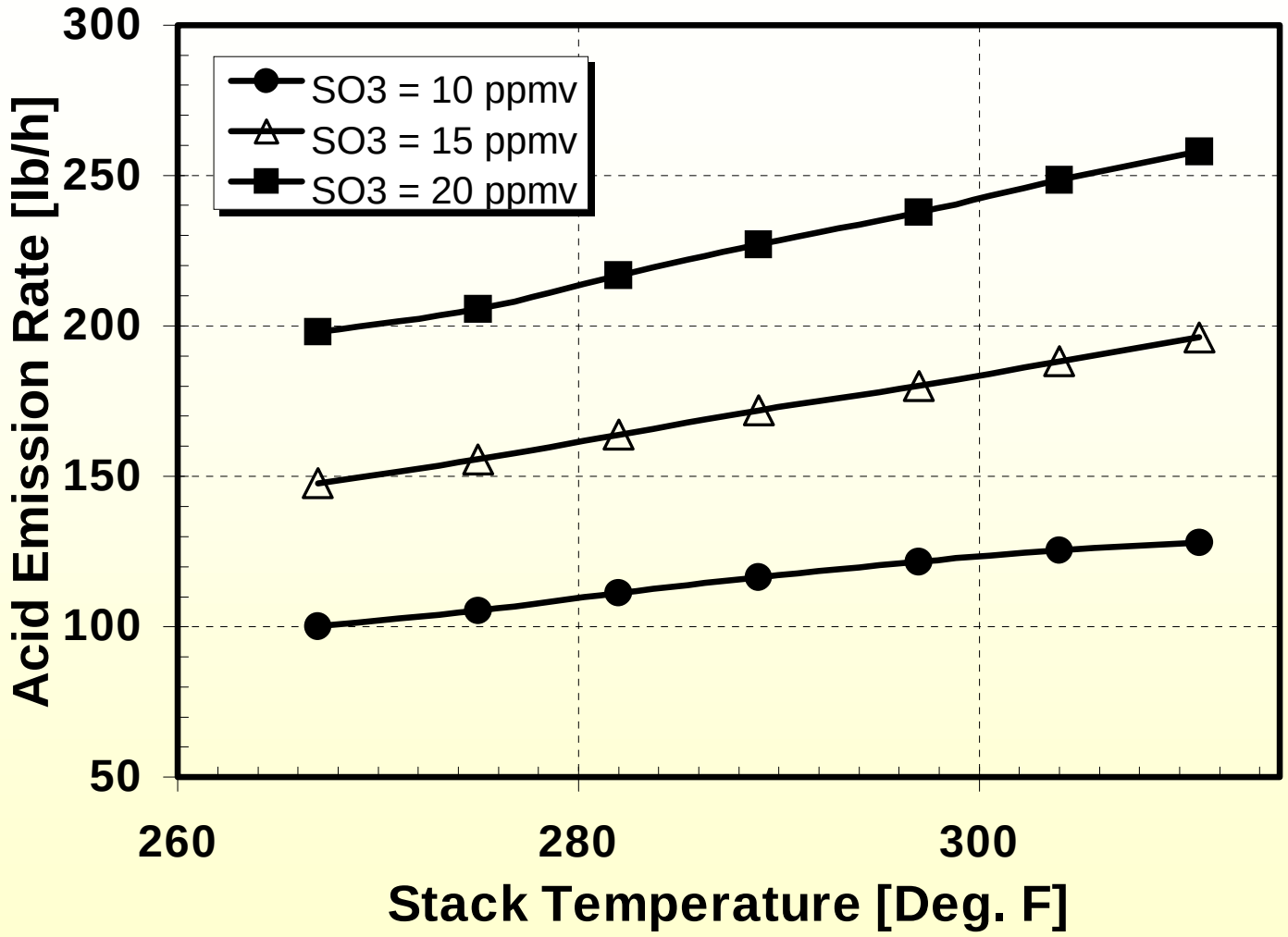


Mp: Mass of One Particle;
Mc: Mass of Condensate on the Particle.

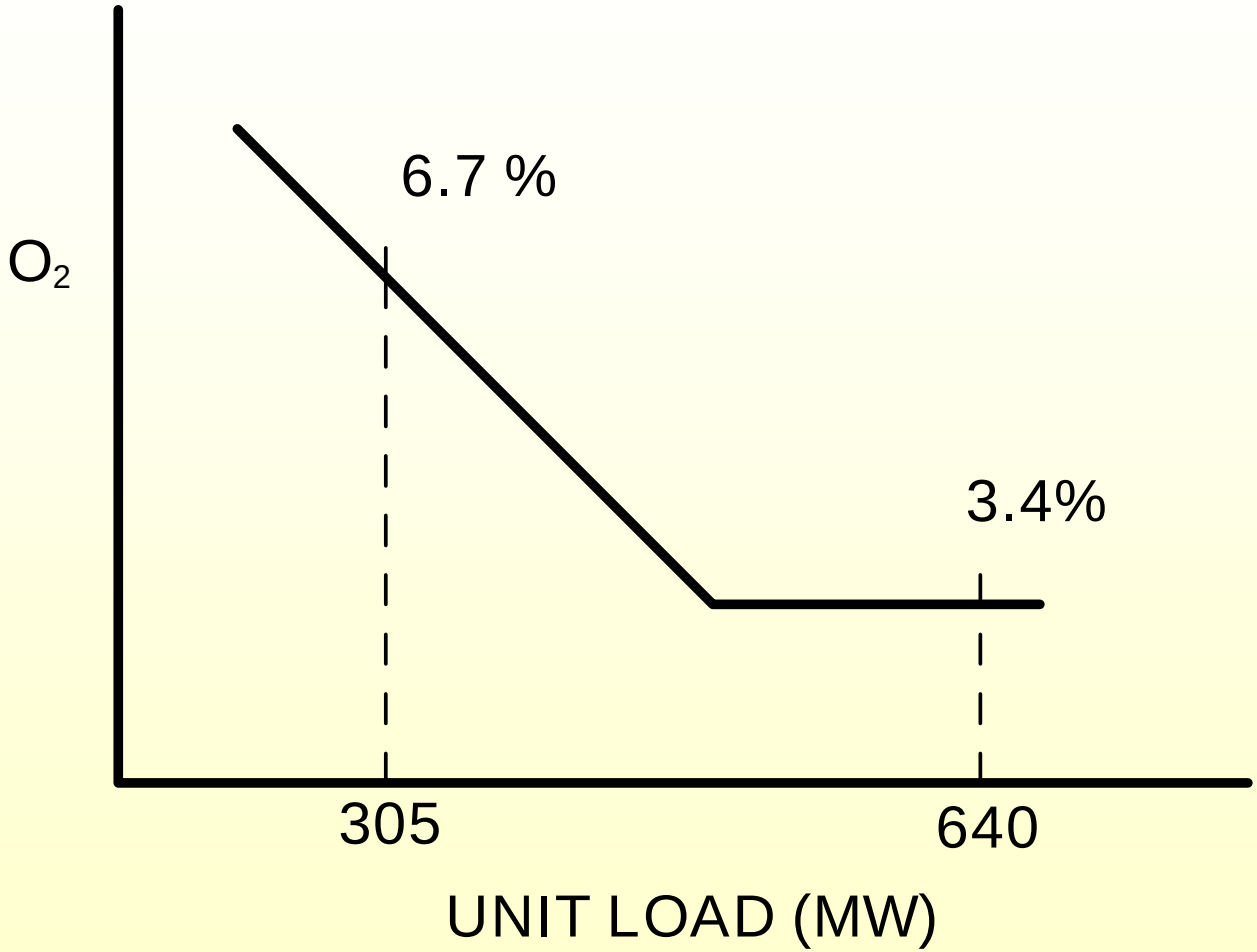
STACK EMISSIONS = [(SO_3 Entering Economizer)

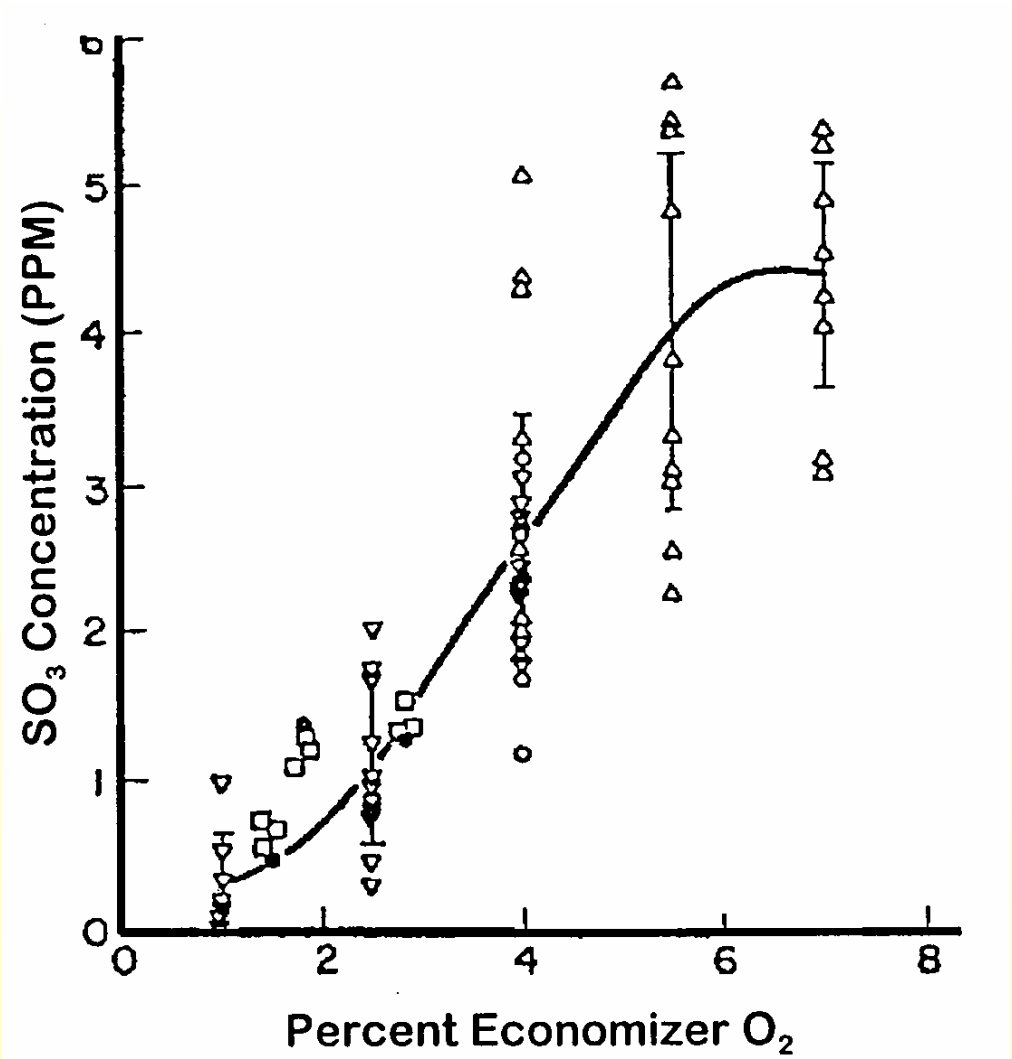
– (Acid Deposited in APH Baskets)

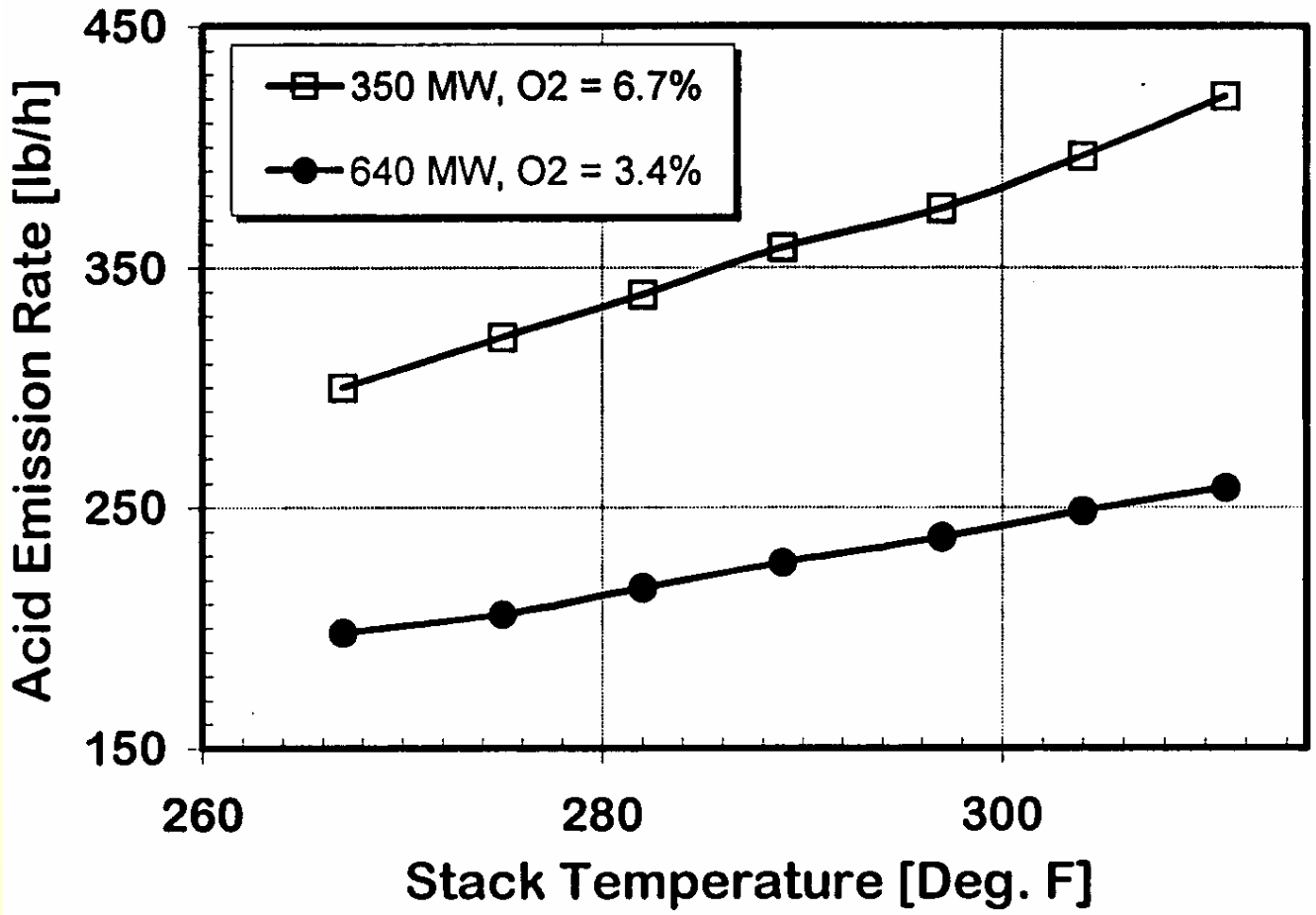
– (Acid Deposited Onto Fly Ash)]



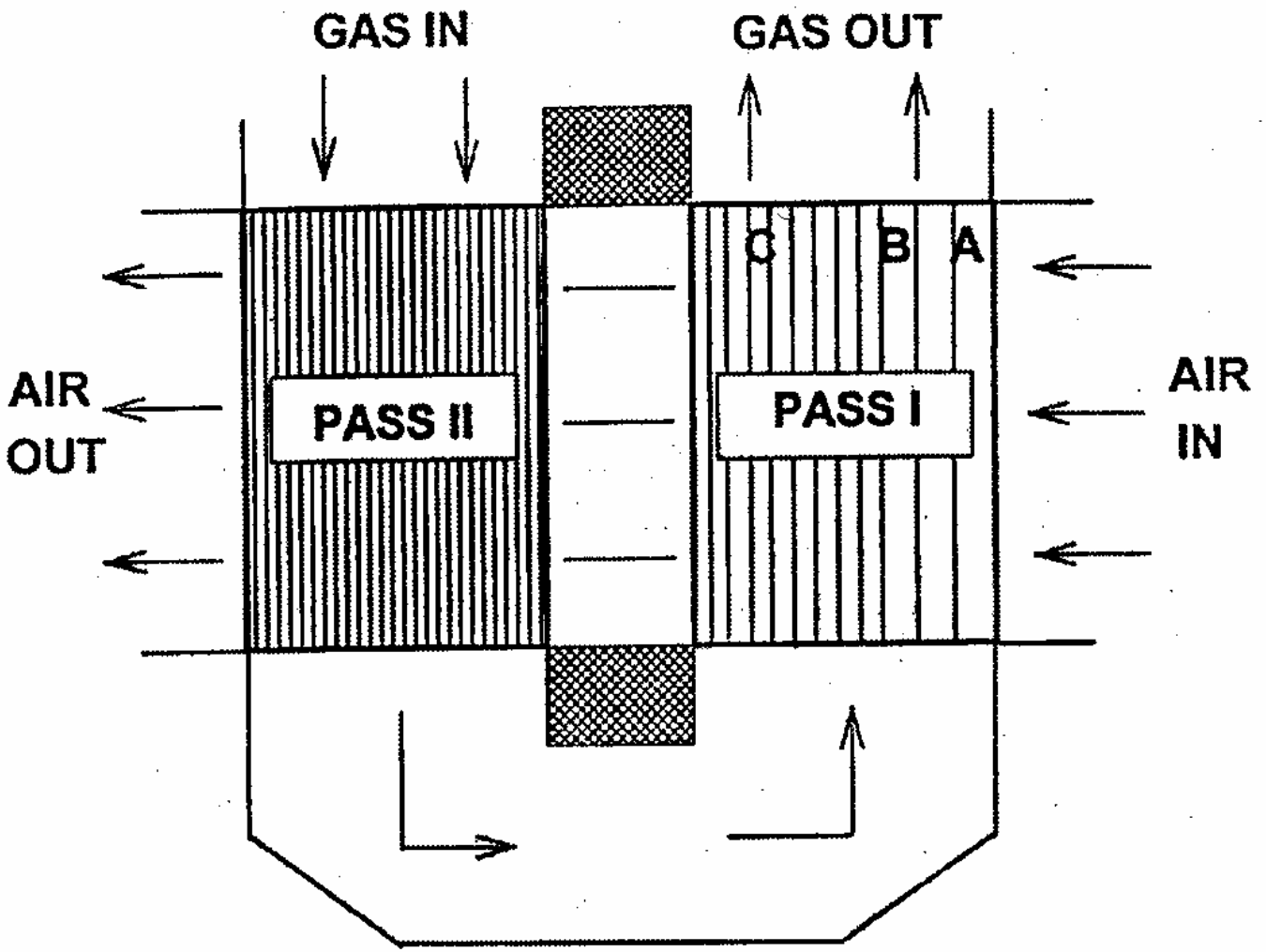
Unit B at 640 MW. (Ljungstrum Air Preheater)


6.7 %
O_2
3.4%
305
640
UNIT LOAD (MW)


SO_3 Concentration (PPM)
0
1
2
3
4
5
6
0
2
4
6
8
Percent Economizer O_2

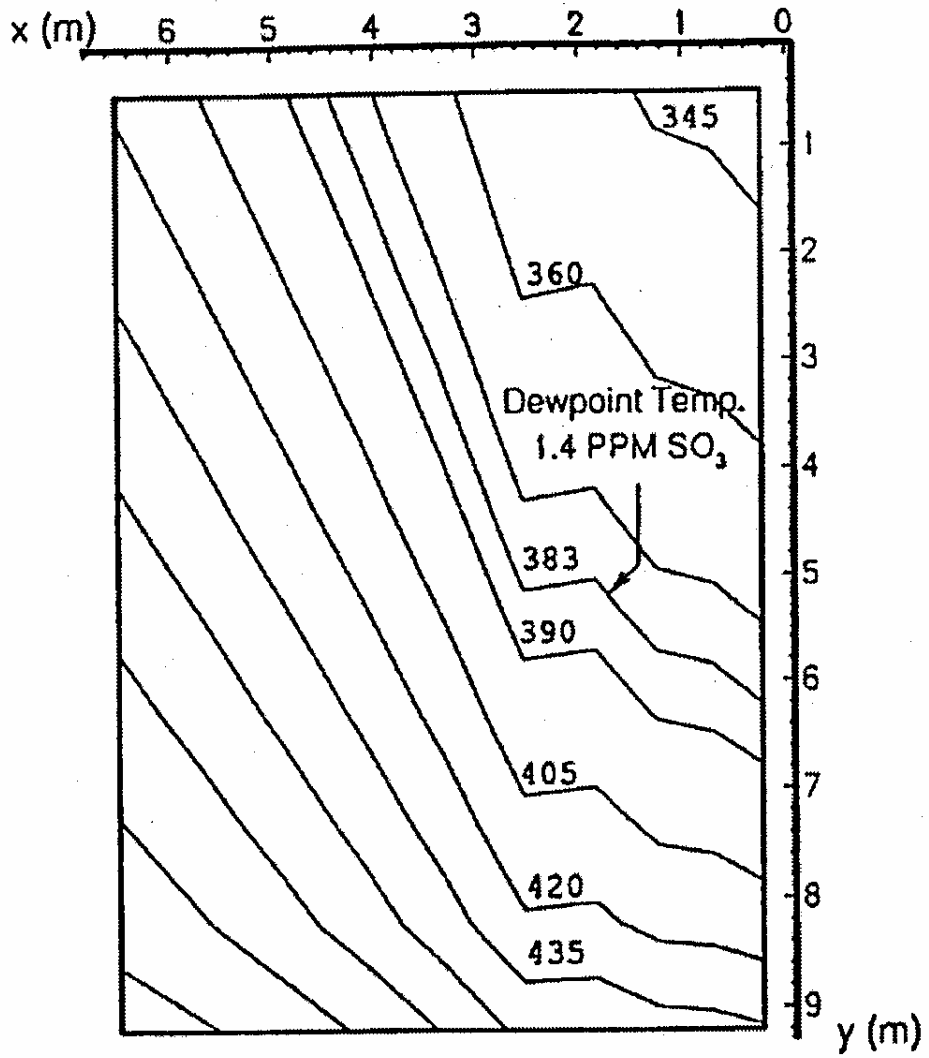


Unit B at 350 MW and 640 MW.
(Ljungstrum air preheater)



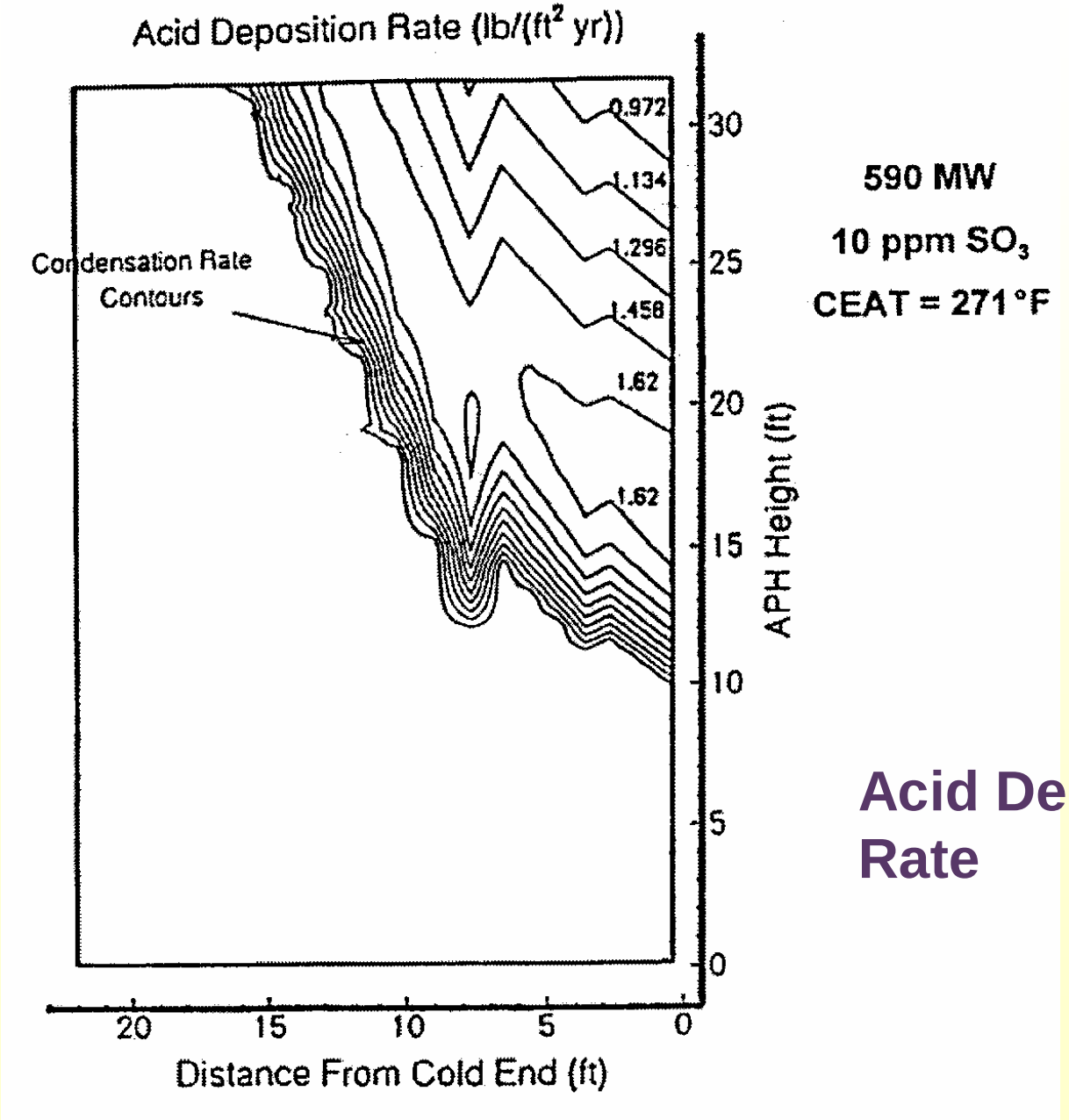
Sketch of a tubular air preheater.

Acid Deposition in a Tubular APH



Metal Temperatures

Acid Deposition in a Tubular APH

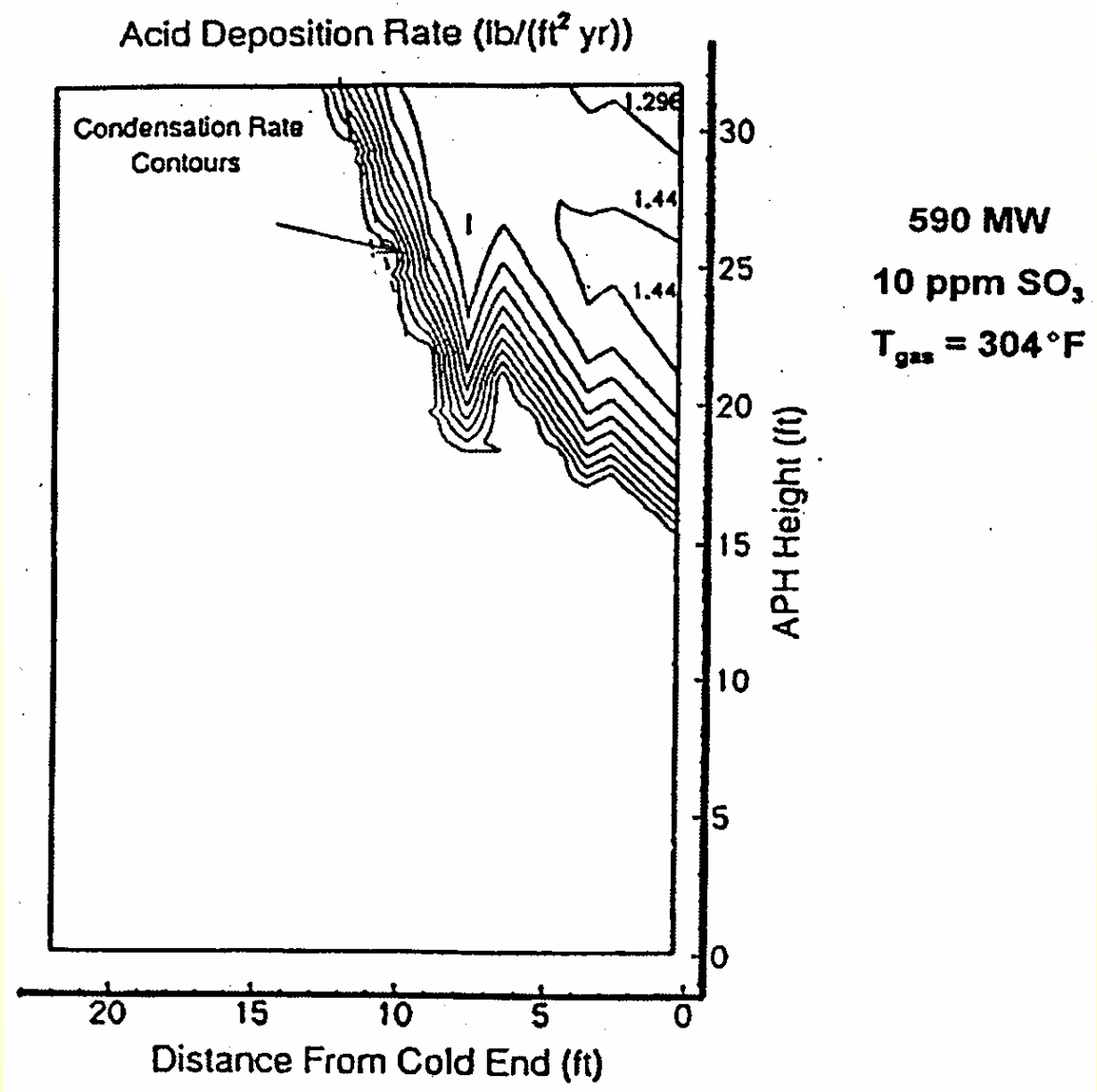


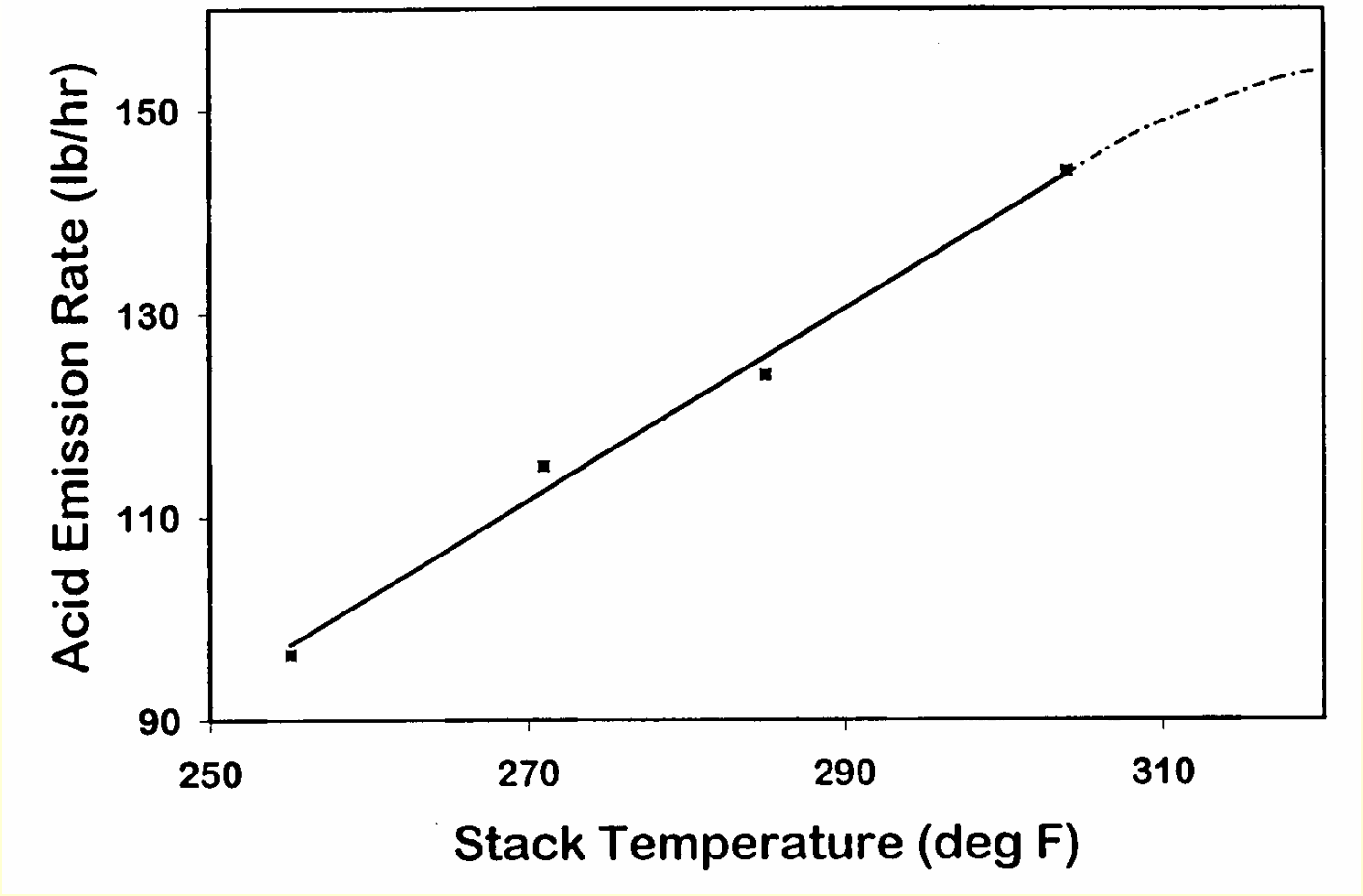
590 MW

10 ppm SO_3

CEAT = 271 °F

Acid Deposition Rate

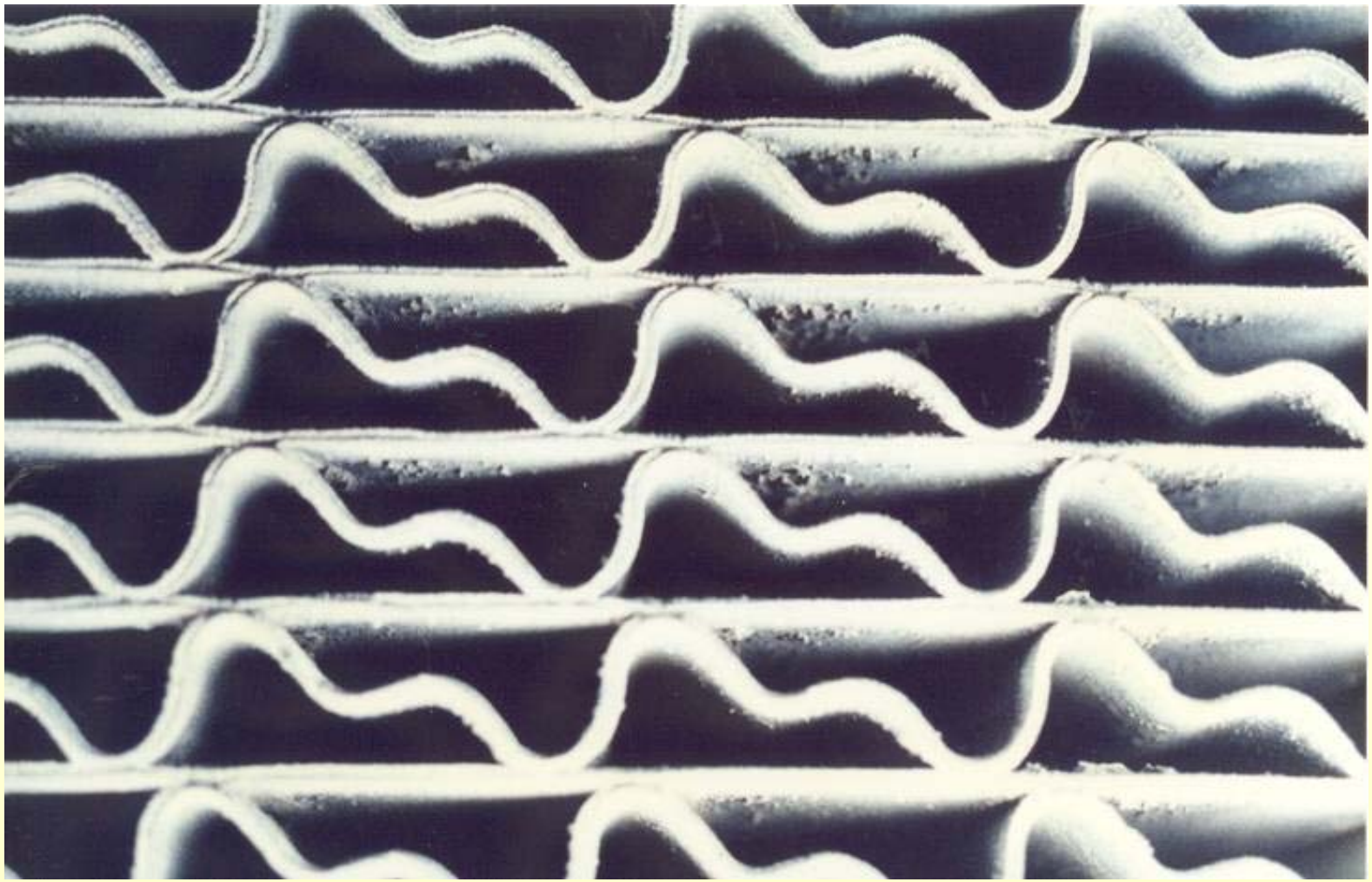

Acid Deposition Rate (lb/(ft² yr))
Condensation Rate Contours
1.296
1.44
1.44
1
30
25
20
15
10
5
0
APH Height (ft)
20
15
10
5
0
Distance From Cold End (ft)
590 MW
10 ppm SO_3
T_{gas} = 304 °F

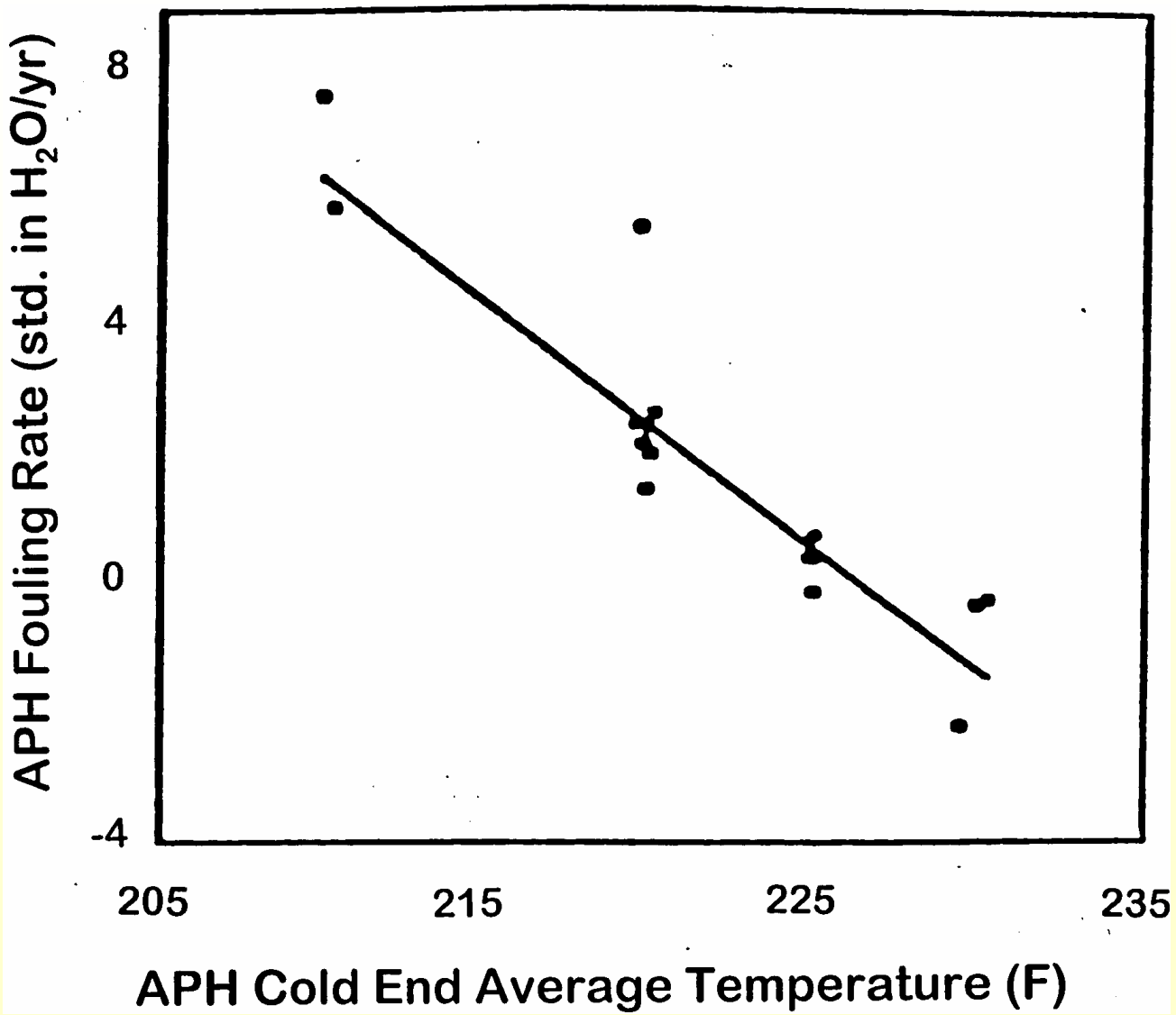


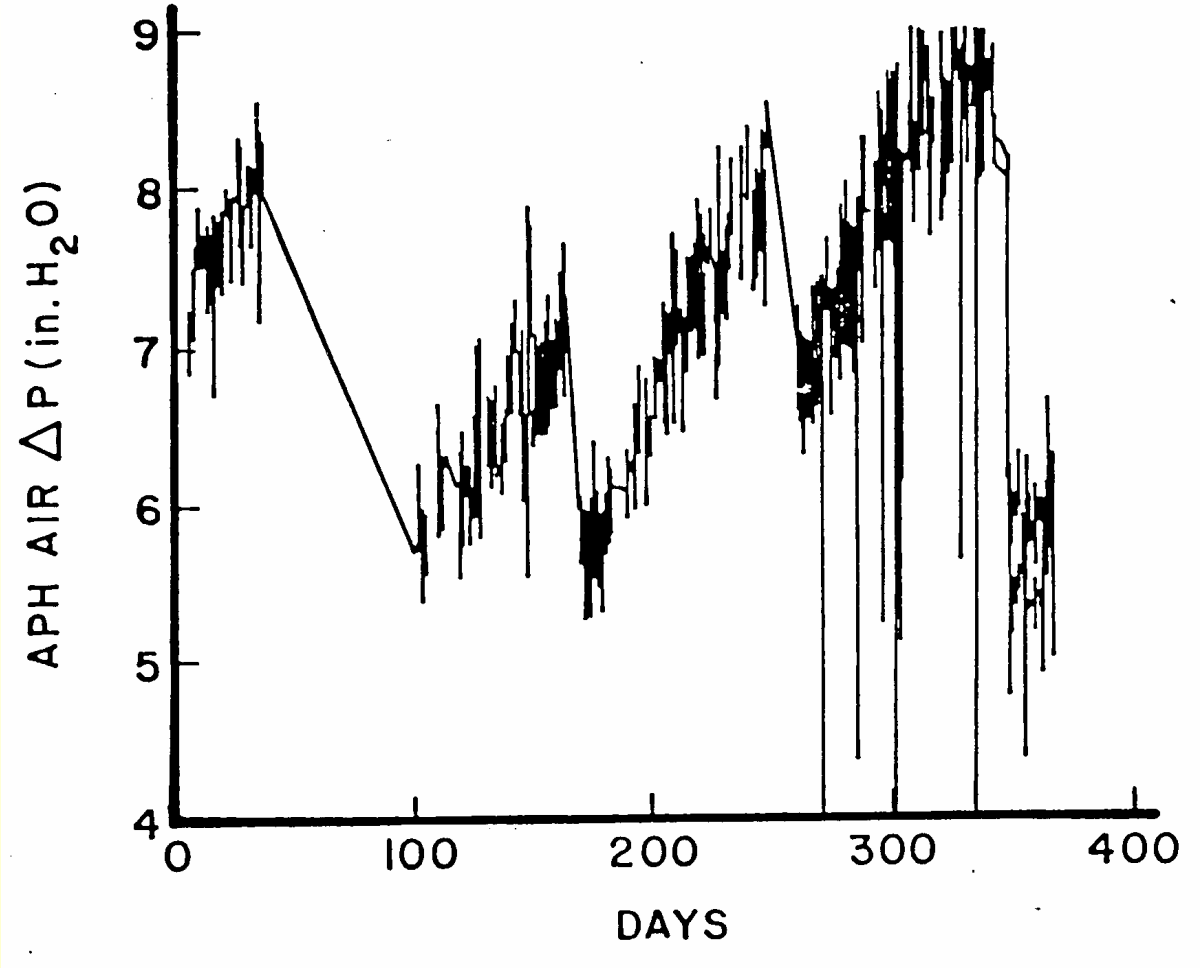
590 MW Unit with a Tubular Air Preheater

CONSEQUENCES OF DECREASING STACK TEMPERATURE

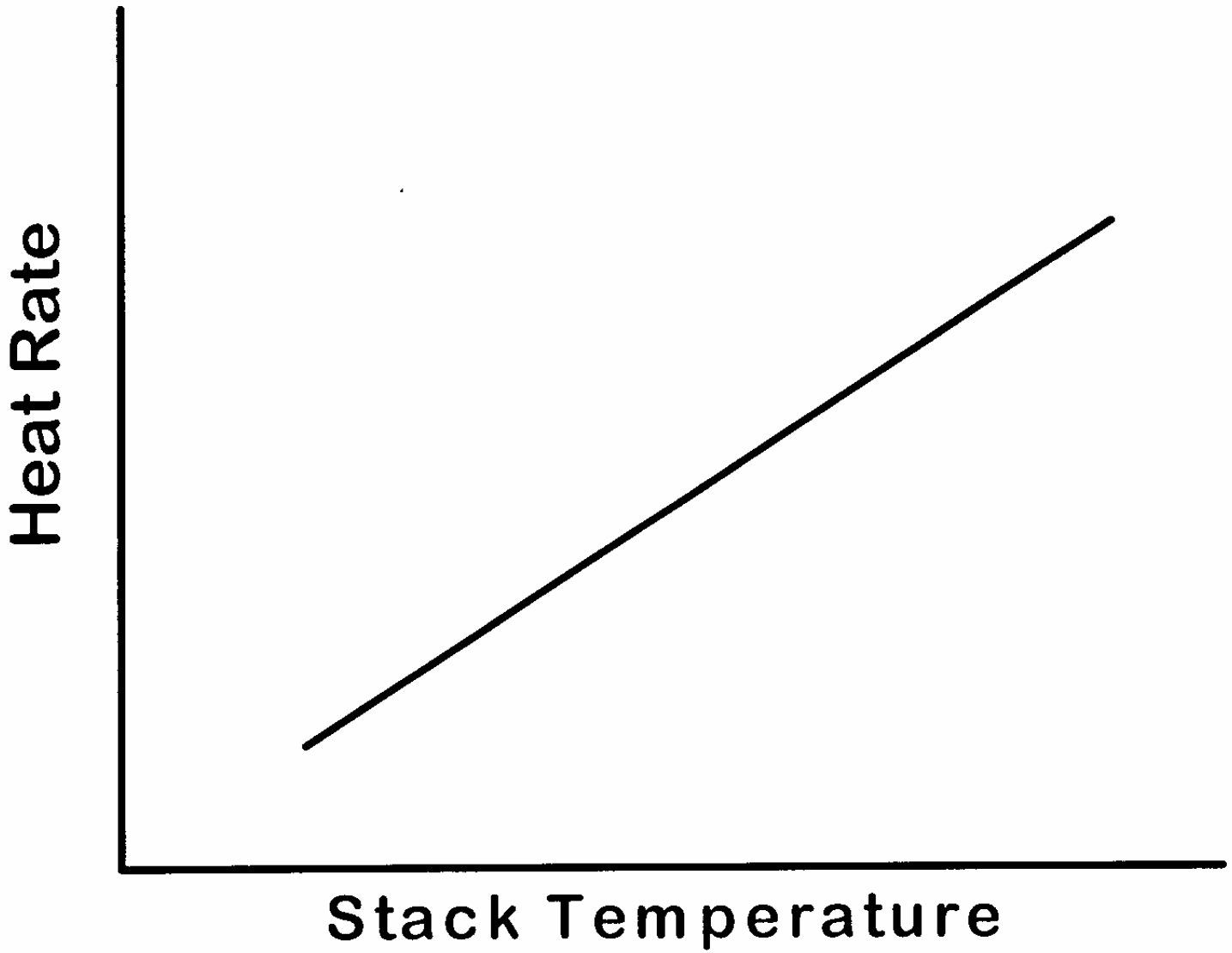
- More Severe APH Cold End Fouling and Corrosion
  - Lost Generation for ID Fan Limited Units
  - Increased Maintenance Costs
- Increased Corrosion in Flue Gas Ducts, ESP and Stack
- Impact on ESP Performance – Could Be Good or Bad
- Improved Heat Rate – Lower Stack Loss

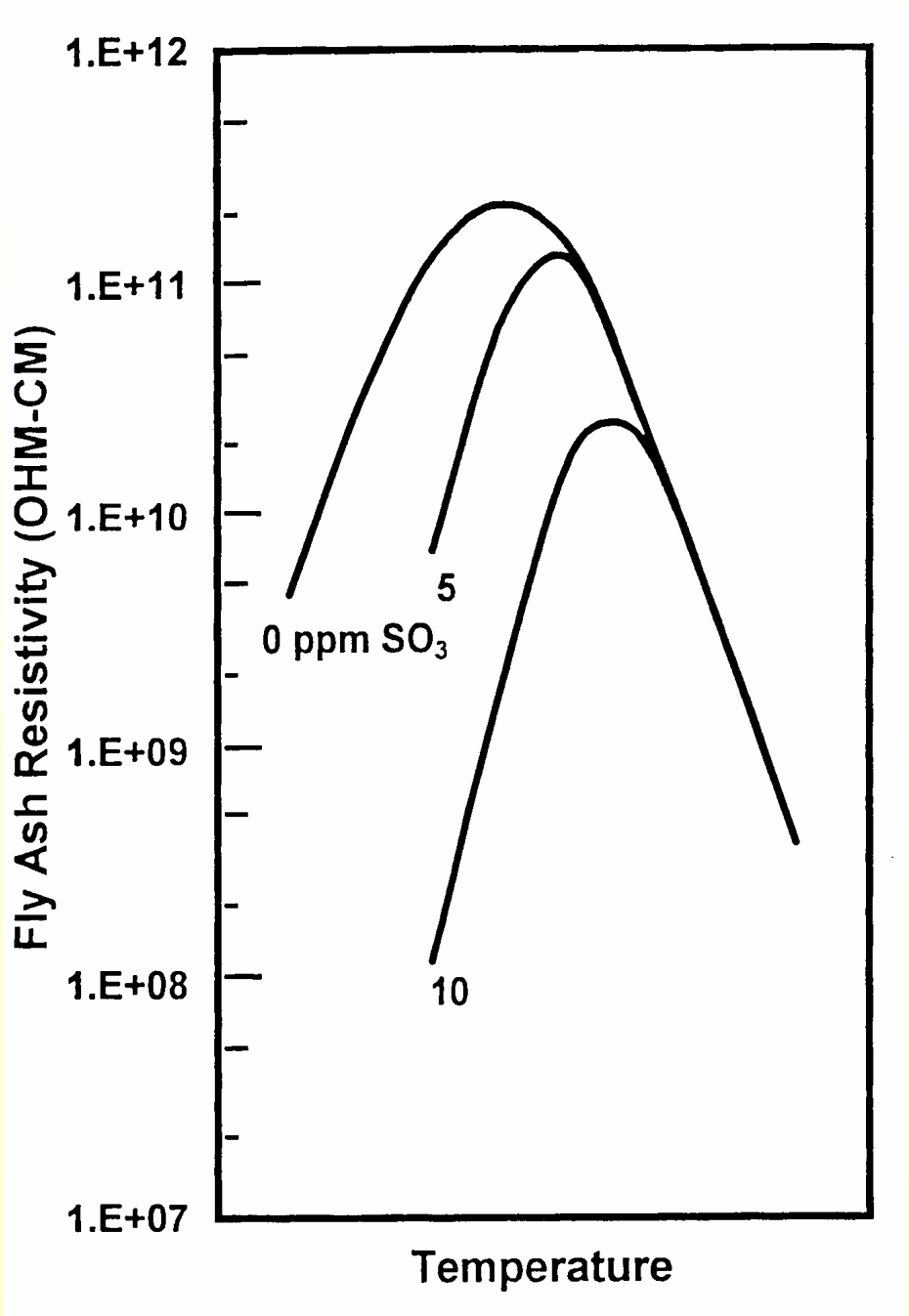



APH Fouling Rate (std. in H_2O/yr)
8
4
0
-4
205
215
225
235
APH Cold End Average Temperature (F)



Typical Plot of APH Air Pressure Drop Versus Time


Heat Rate
Stack Temperature


1.E+12
1.E+11
1.E+10
1.E+09
1.E+08
1.E+07
Fly Ash Resistivity (OHM-CM)
0 ppm SO_3
5
10
Temperature

CONCLUSIONS

Acid Emissions – Strong Function of:

- Boiler and SCR Design
- Fuel Sulfur and Ash Content
- Operating Conditions

Emissions Vary with:

- Unit Load
- Economizer O_2
- SCR Gas Inlet Temperature
- Air Preheater Exit Gas Temperature