Power Plant Pollution Controls

Green Chemistry Fall 2007

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Power Plant Pollution Controls

1. Power plants and fuels
2. Emission control technologies
3. Are pollution controls green?

Fuels

- Coal is by far the most likely to produce pollution.
- Cleanest to least clean coal types:
  - Anthracite
  - Bituminous
  - Sub-bituminous
  - Lignite
- Natural gas can contain some sulfur, but otherwise is very clean. Only NO_x controls must be used.

Bituminous Coal

USGS/Minerals in Your World

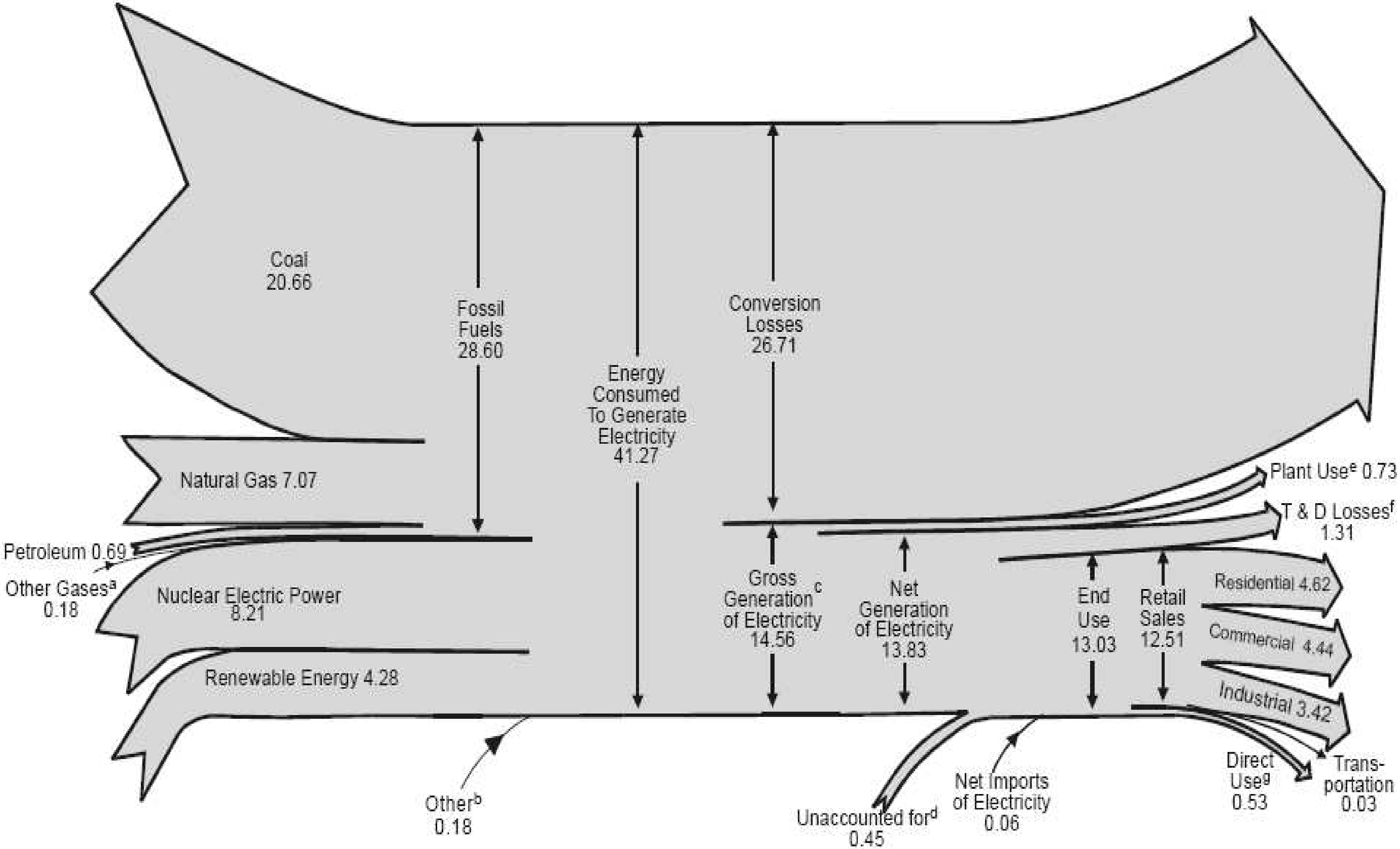


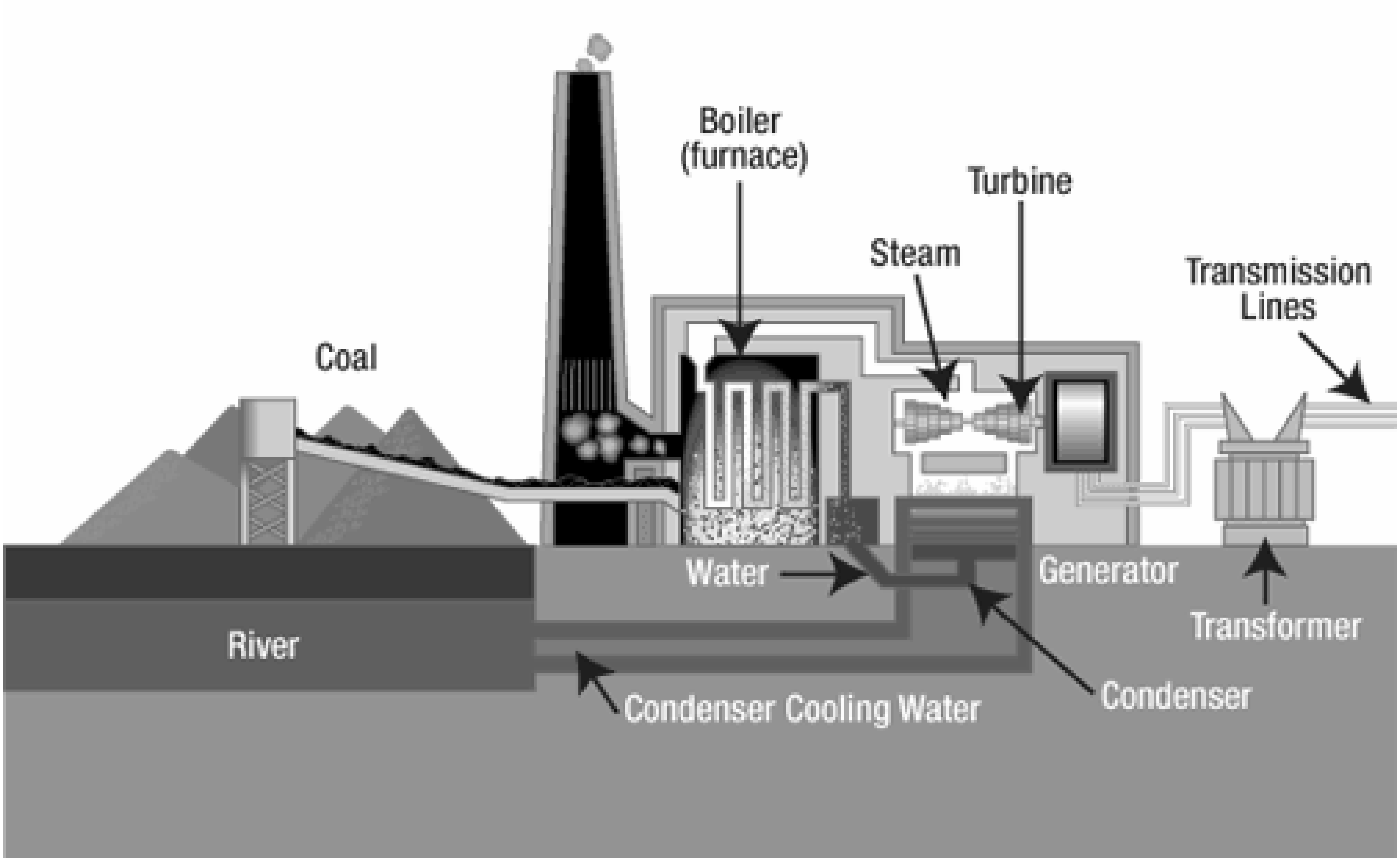
Figure from EIA Annual Energy Review 2006
http://www.eia.doe.gov/emeu/aer/diagram5.html

US Electricity Energy Flow

All numbers are in quadrillion (10^{15}) BTU (1 BTU ≈ 1.05 kJ)

Coal power plant designs

- Pulverized coal steam boiler
  - High-quality coal is crushed, then burned.
  - Traditional design
- Fluidized-bed
  - Burns at lower temps with limestone directly.
  - Minimizes SO_2 and NO_x emissions
- Coal gasification
  - Coal is exposed to hot steam and low O_2 conditions.
  - Organic molecules decompose to form syngas.
  - Using gas turbines allows better efficiency.
- All data here is for electricity-generating power plants.



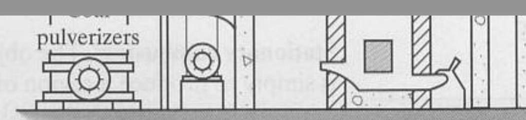


Figure 7-1 Schematic diagram of a typical pulverized coal steam boiler for the generation of electrical power. (Babcock and Wilcox, 1978)

http://www.tva.gov/power/coalart.htm

Heinsohn, R. J. *Sources and Control of Air Pollution.* New York: Prentice Hall, 1998.

Major Pollutants

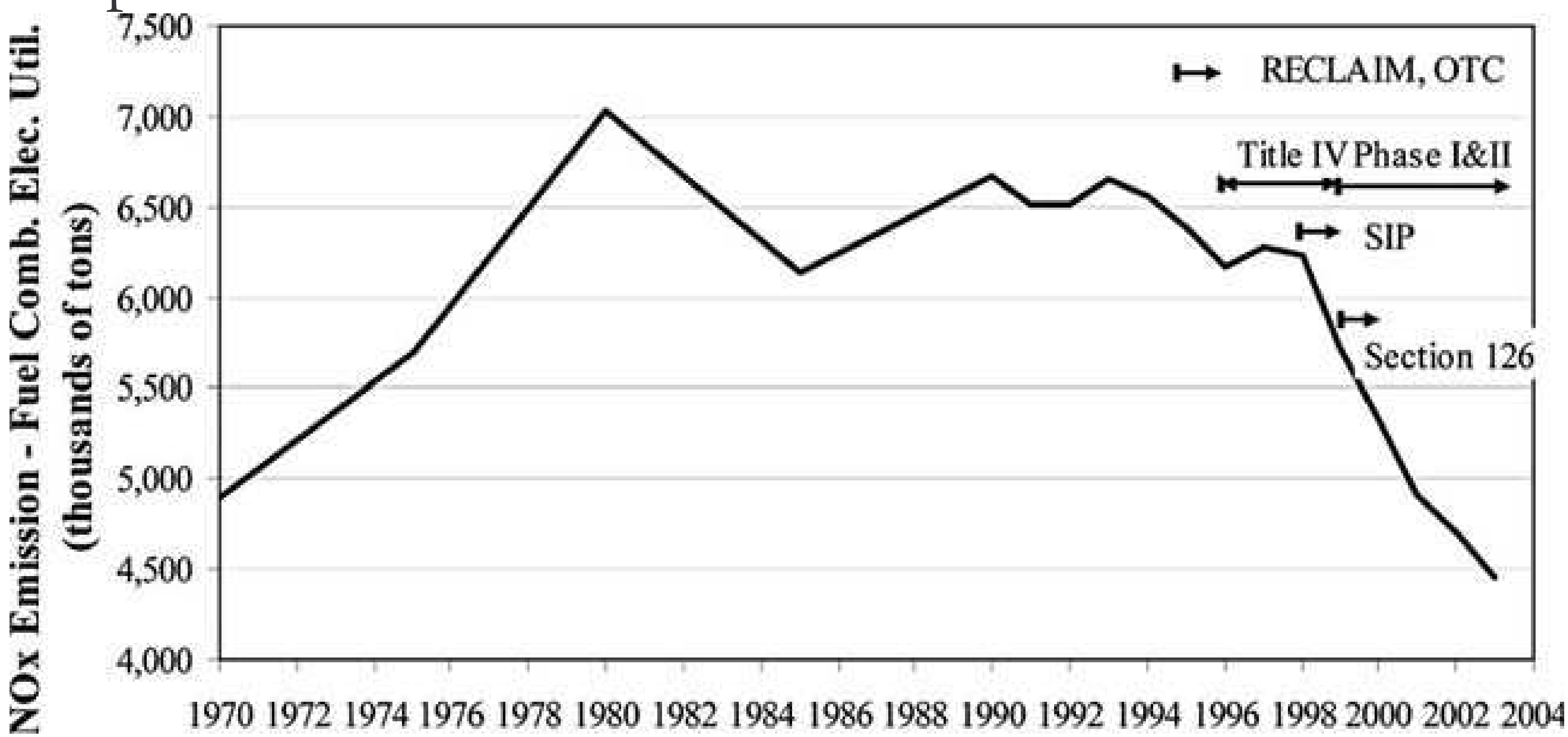
- **Nitrogen oxides (NO_x)** –from high heat oxidation of atmospheric nitrogen in combustor
- **Sulfur dioxide** – formed from oxidation of sulfur compounds in coal (pyrite and organic)
- **Mercury** – amount depends on the type of coal used
- **Particulates** – includes ash, carbon, and sulfur-containing aerosols
- **Carbon dioxide**

Pollution effects

- Acid rain
- Photochemical smog
- Respiratory disease
- Mercury poisoning
- US Clean Air Act passed 1963
  - Amended in 1967, **1970**, 1977, 1990, 1996.

NO_x and Government Regulation

- Government regulations were the driving force behind development of NO_x controls.
- Cost reductions are proportional to technology adoption.



Yeh, Rubin, Taylor, and Hounshell *J. Air & Waste Manage. Assoc.* **55**:1827–1838

Ways to control pollution

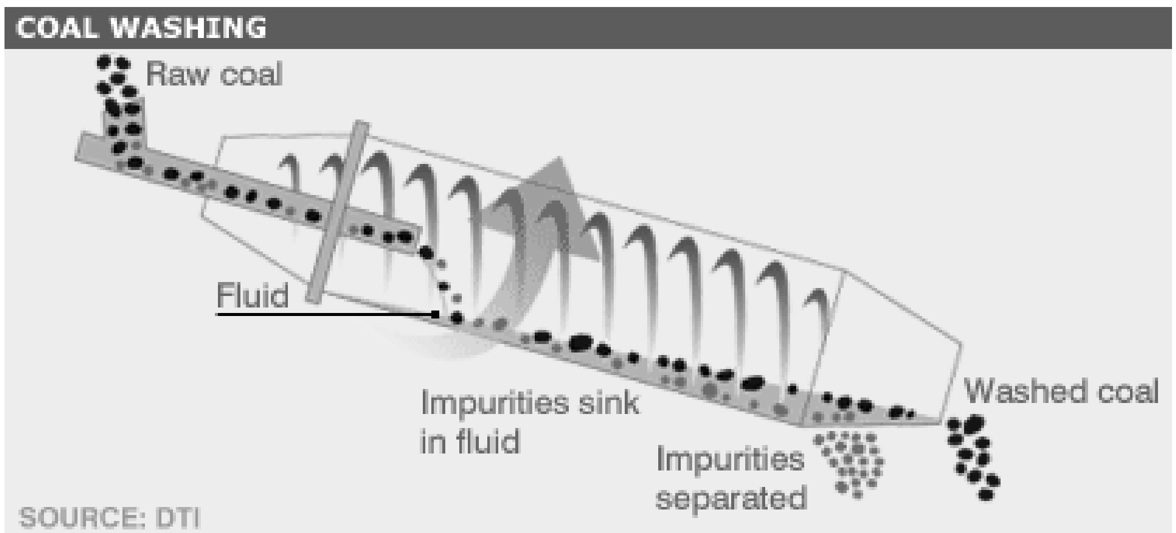
- Fuel type and pretreatment
- Combustor alterations
  - Optimization of conditions and inputs in steady state
  - Re-feed inert flue gases into system to dilute oxygen
- Flue gas controls
- Effective measurement of pollution emission

Considerations when adopting control technologies

- Cost to build and maintain
- Energy usage
- Reagents needed to operate
- Byproducts - usable or dumped?
- Effectiveness
- Effect on multiple pollutants – some control technologies can control more than one pollutant.

Coal pretreatment

- Coal washing – grind coal into small pieces and use density to separate it from other minerals.



BBC, http://news.bbc.co.uk/1/hi/sci/tech/4468076.stm

Combustor Alterations

- Optimization of conditions and inputs in steady state
- Re-feed inert flue gases into system to dilute oxygen

Flue Gas Control Technologies

- Catalytic reduction
- Scrubbers
- Particulate Controls
  - Fabric bag filters
  - Vortex and drop tray
  - Electrostatic precipiators
- Oxidizing/reducing agents
- Adsorbents
- Carbon sequestration

Acronyms

- FGD – flue gas desulfurization
- PCD – particulate control devices
- SCR – selective catalytic reduction
- ESP – electrostatic precipitators
- LNB – low NO_x burner
- CT – control technology
- CFB – circulating fluidized bed

NO_x

Sources of NO_x

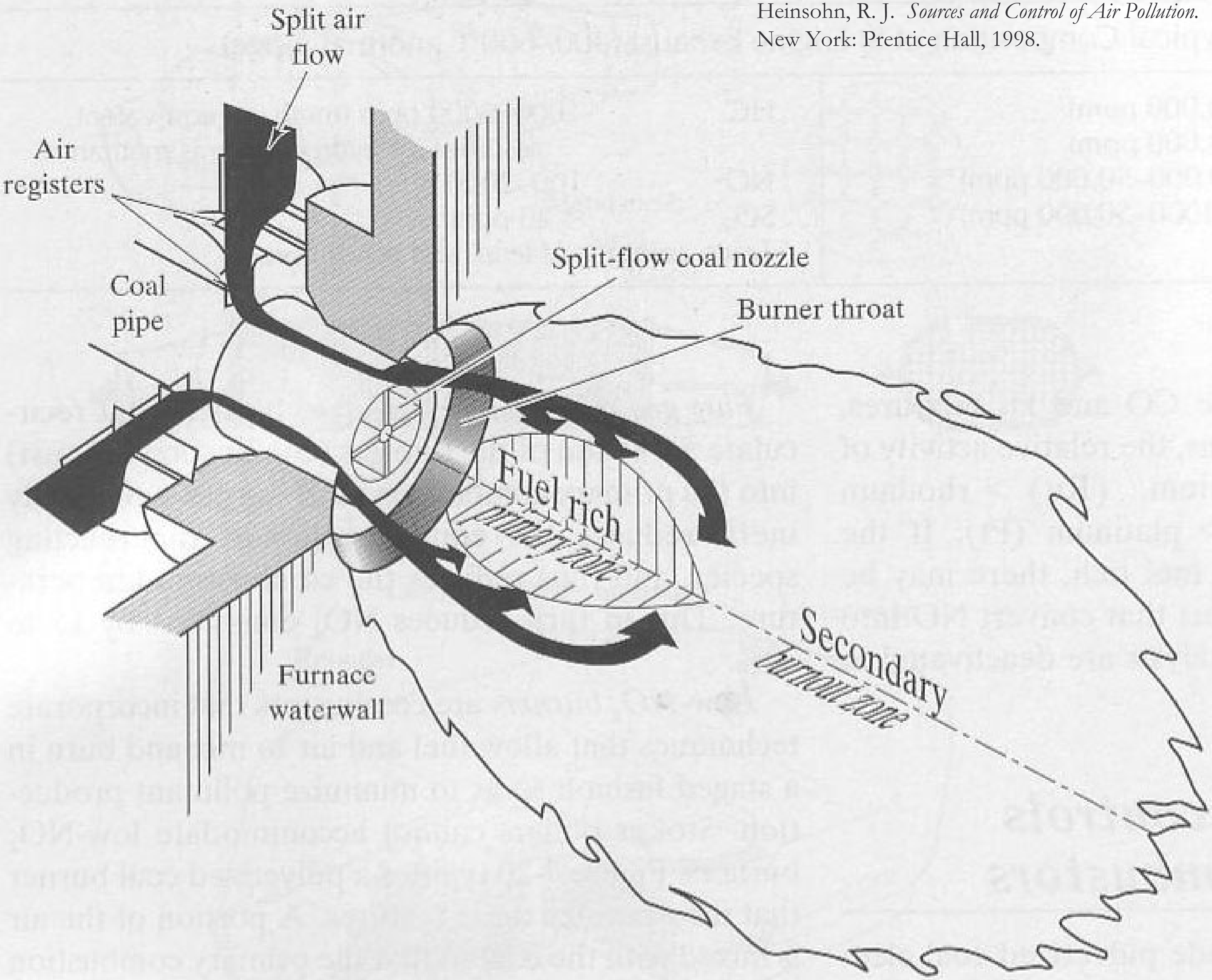
- Thermal NO_x
  - Formed by high temperature oxidation of atmospheric nitrogen
  - Very sensitive to peak temperature (reciprocating engines)
  - 85% of total NO_x
- Prompt NO_x
  - Made in reactions of N_2 and flame-produced hydrocarbon radicals
  - Occurs in fuel-rich areas of combustor
- Fuel NO_x – formed from nitrogen in the fuel

Combustor Modifications

1. Combustor geometry optimization
2. Flue gas recirculation
   - Dilutes fuel/air mix with flue gas (O_2 conc 3.3% is standard)
3. Low NO_x burners (LNB)
   - A type of staged combustion, using fuel-rich and fuel-lean zones to reduce peak temp.

- These are the least expensive options
- All work by reducing fuel burning temperature

Heinsohn, R. J. *Sources and Control of Air Pollution.* New York: Prentice Hall, 1998.



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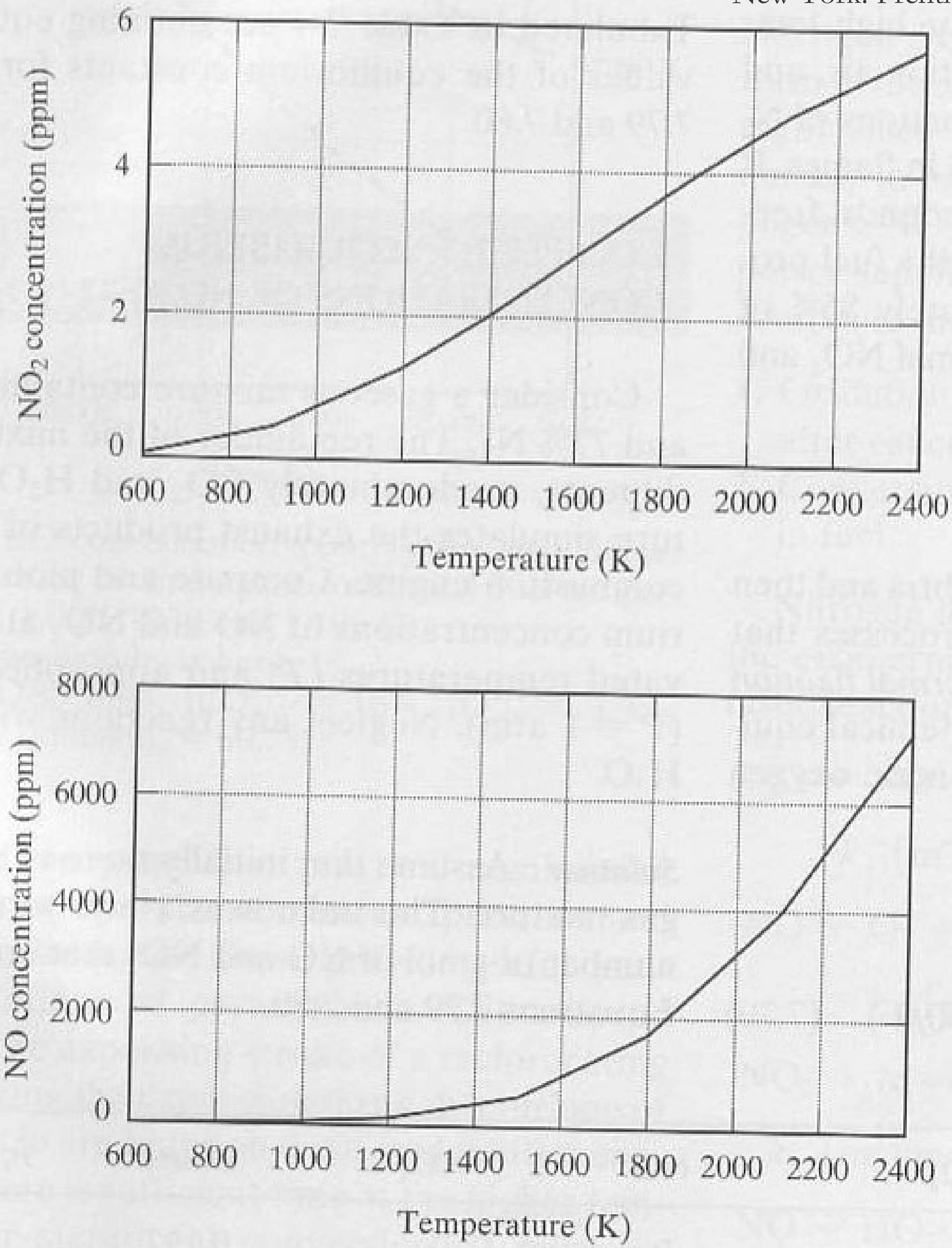


Figure E7-5 Equilibrium concentrations (ppm) of NO_2 and NO versus temperature (K). Initial conditions % by volume: $[N_2]_0 = 77\%$, $[O_2]_0 = 3.3\%$, [diluent] = 19.7%, Pressure = 1 atm

SCR – Selective Catalytic Reduction

- The reaction of NO_x and NH_3 (or urea) with a catalyst bed at high temperature.

$$\mathbf{NO_x + NH_3 + O_2 \rightarrow N_2 + H_2O}$$

- Pros & Cons:
  - Eliminates 70-90% of NO_x
  - Expensive catalyst with high replacement cost
  - Stoichiometric ammonia or urea is required
  - High sulfur content in flue gases can poison catalyst
  - Can be done non-catalytically (SNCR)

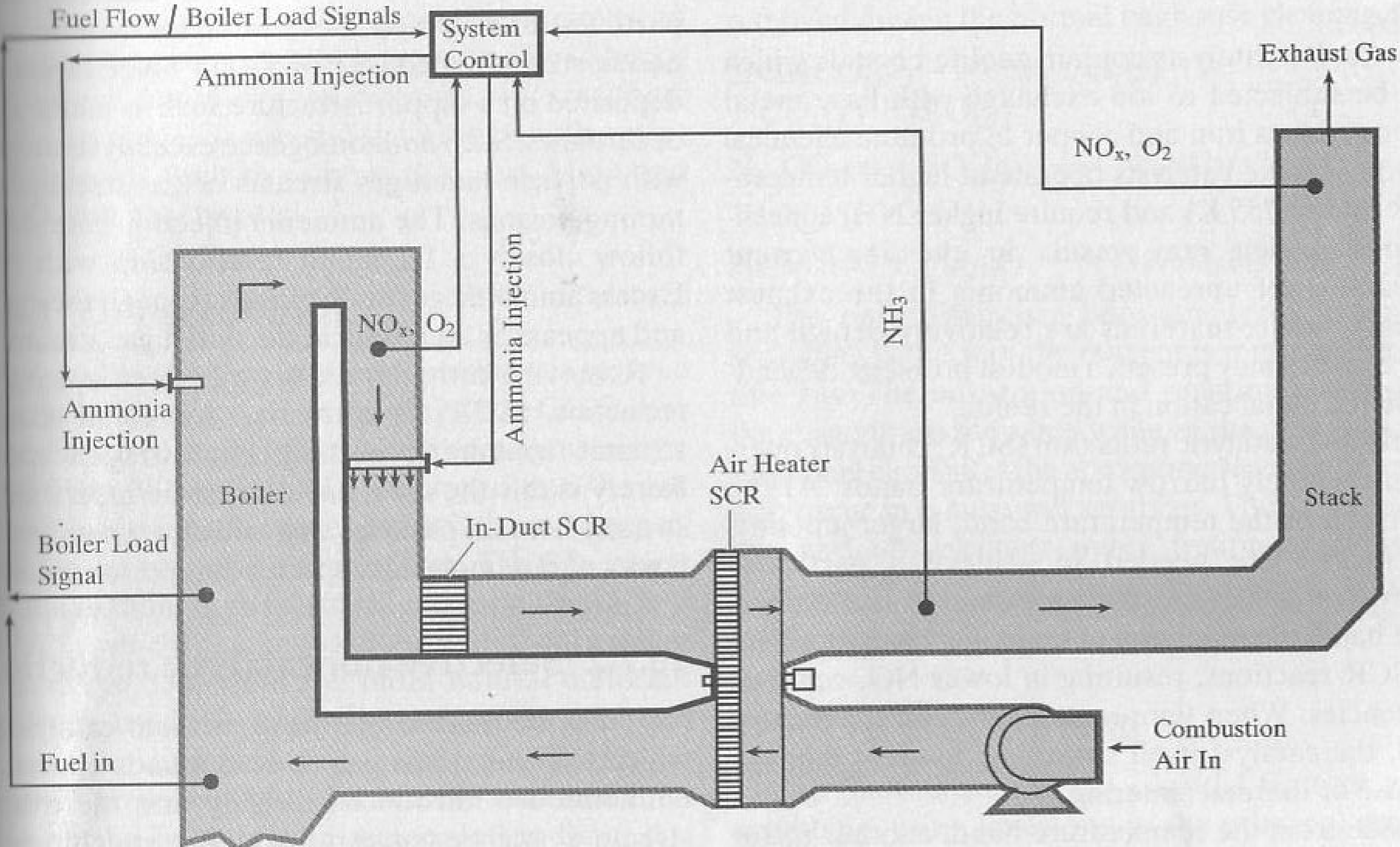


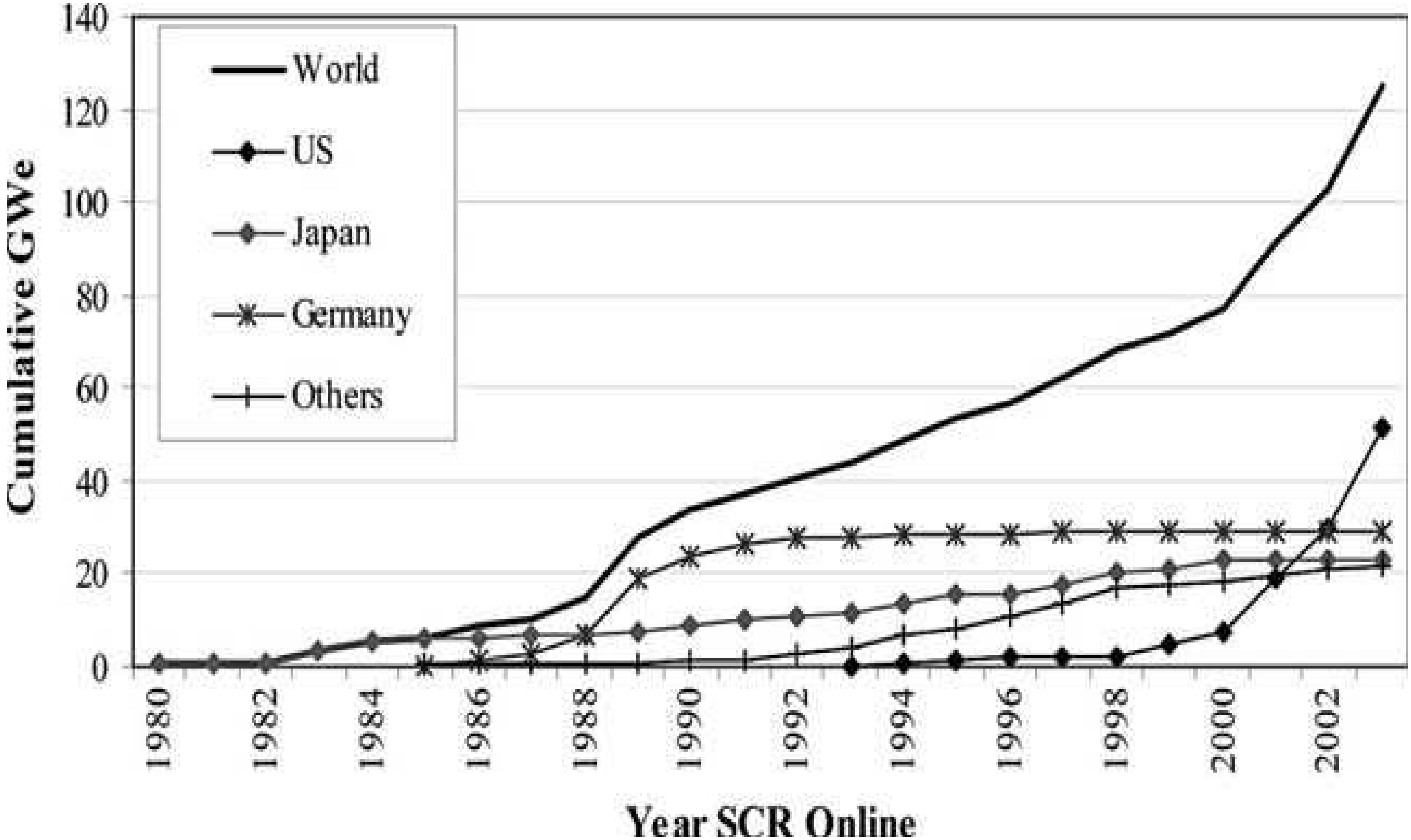
Figure 10-27 Schematic diagram of staged thermal reduction of NO_X for an electric utility boiler showing nonselective catalytic ammonia injection (NSCR) and in-duct and air-heater applications of selective catalytic reduction (SCR) (with the permission of *Wahlco*)

Heinsohn, R. J. *Sources and Control of Air Pollution.* New York: Prentice Hall, 1998.

SCR Catalysts

- Noble metal catalysts (Pt/Al_2O_3) at low temp
  - Easily poisoned and corroded by sulfur compounds (used in natural gas plants only)
  - Lower Temp
- Base metal catalysts (V_2O_5/TiO_2/other metals)
  - Poisoned by particulates, acids, some metal oxides
  - Toxic: special disposal required
- Zeolites (zeolite/Cu/Fe)
  - High Temp, more NH_3 required

SCR capacity



J. Air & Waste Manage. Assoc. **55**:1827–1838

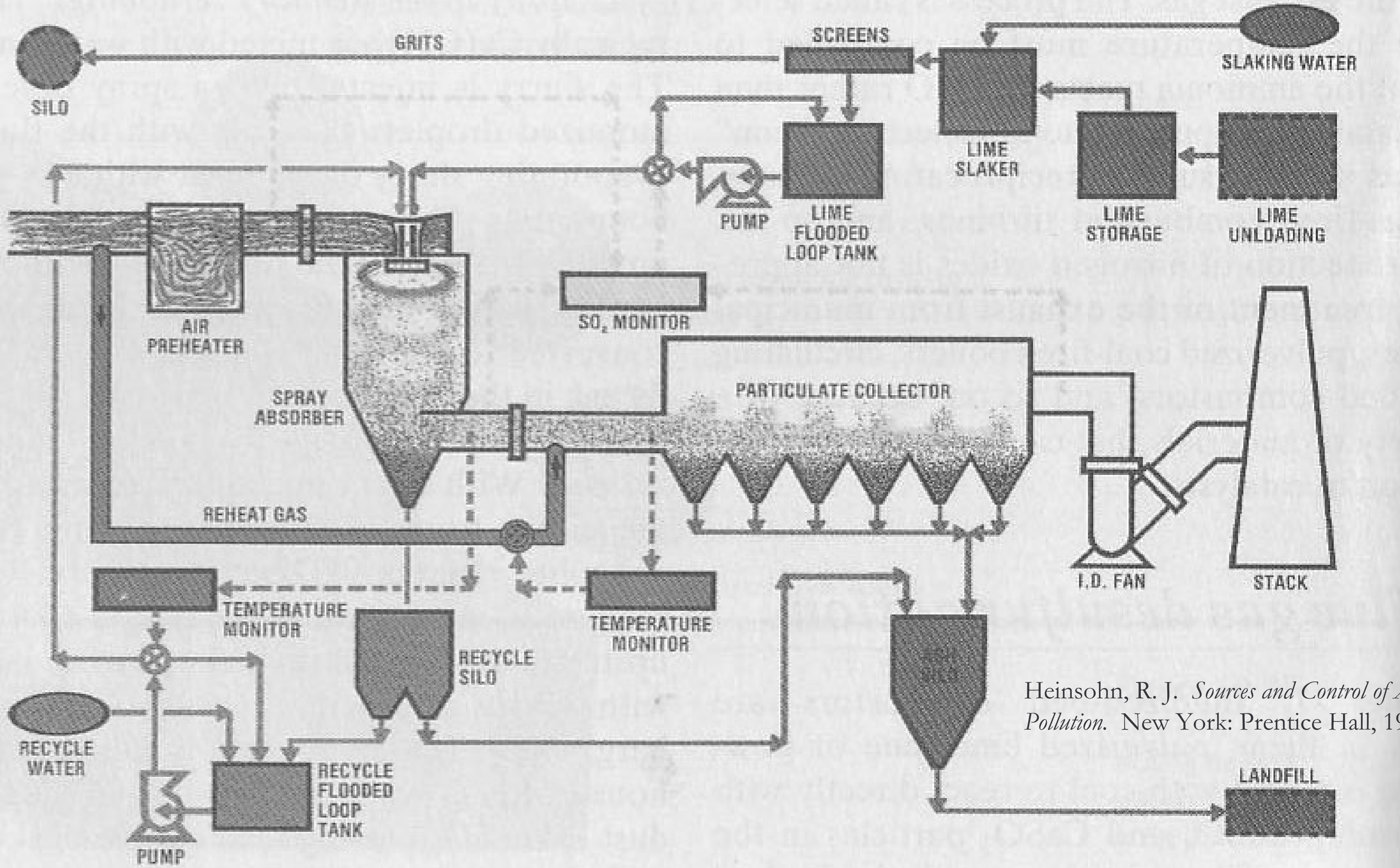
Reduction of NO_x

Technology	Yeh, Rubin, Taylor, and Hounshell
Combustor alterations	30-60%
SNCR	30-50%
SCR	70-90%

SO_2

SO_2 Flue Gas Scrubbing

- Dry scrubbing
  - $Ca(OH)_2$ slurry droplets or solid $NaCO_3$ particles are injected in flue gas stream
  - $CaSO_4$ or Na_2SO_4 particles are captured by fabric filters with fly ash
- Wet scrubbing
  - Limestone slurry reacts to form $CaSO_3$, then $CaSO_4$
  - Corrosive low pH and scaling are produced
  - Large amounts of waste sludge are produced.



Heinsohn, R. J. *Sources and Control of Air Pollution.* New York: Prentice Hall, 1998.

Figure 10-29 Schematic diagram of the GE Dry Flue Gas Desulfurization System using lime to remove SO_2. The lime reagent enters the system as a slurry. Hot flue gas evaporates water from the slurry and SO_2 is adsorbed on the remaining particles of dry reagent. Flyash and the dry reagent are collected by a fabric filter. Additional SO_2 is adsorbed as the flue gas passes through the dust cake containing the dry reagent particles. (Figure used by permission of General Electric Environmental Services, Inc.)

Limestone Slurry Forming

- Limestone ($CaCO_3$) is converted to form more reactive and soluble calcium hydroxide.

$$\mathbf{CaCO_3 + heat \rightarrow CaO + CO_2}$$

$$\mathbf{CaO + H_2O \rightarrow Ca(OH)_2}$$

- Calcium hydroxide or limestone reacts with sulfur dioxide.

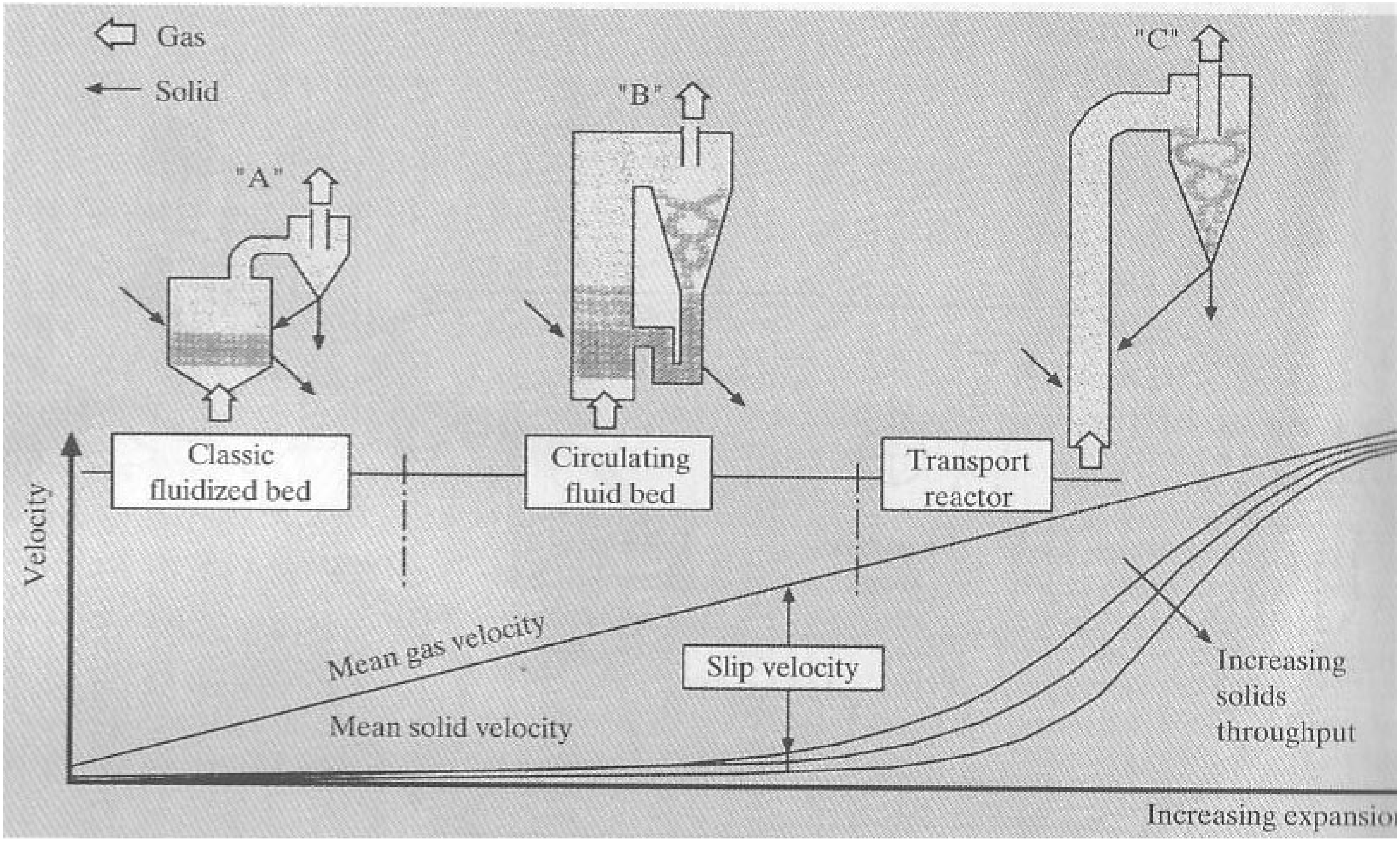
$$\mathbf{CaCO_3 + SO_2 + 2\ H_2O \rightarrow CaSO_3{\bullet}2H_2O + CO_2} \text{ or}$$

$$\mathbf{CaO + SO_2 + 2\ H_2O \rightarrow CaSO_3{\bullet}2H_2O}$$

- $CaSO_3$ converts to sulfate in acidic environments with oxygen.

Fluidized Bed Combustors

- Solid coal pieces are uplifted by gas coming from the bottom and burned in.
- Limestone ($CaCO_3$) or dolomite ($MgCO_3$) is added to the dry fuel, which captures sulfur before it leaves the combustor (up to 90%). Na, K, $CaCl_2$ added to increase adsorption.



Heinsohn, R. J. *Sources and Control of Air Pollution.* New York: Prentice Hall, 1998.

Advantages of FBT

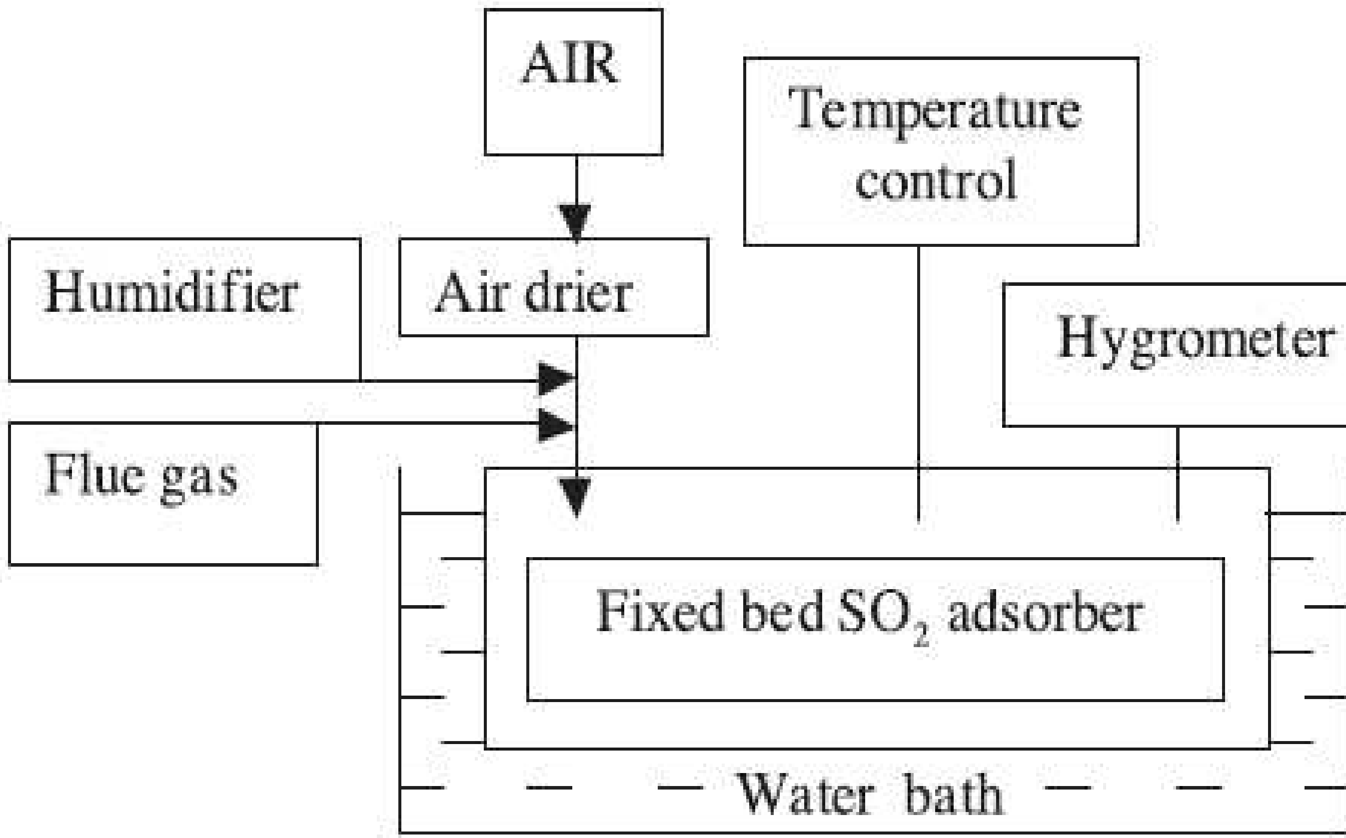
- Uniform, lower temperature throughout the bed
- Complete mixing of fuel and limestone provides good SO_2 reduction
- Large interface between gas and solid
- Lower temperatures means much less NO_x
- Lower-quality coal and other fuels can be burned.

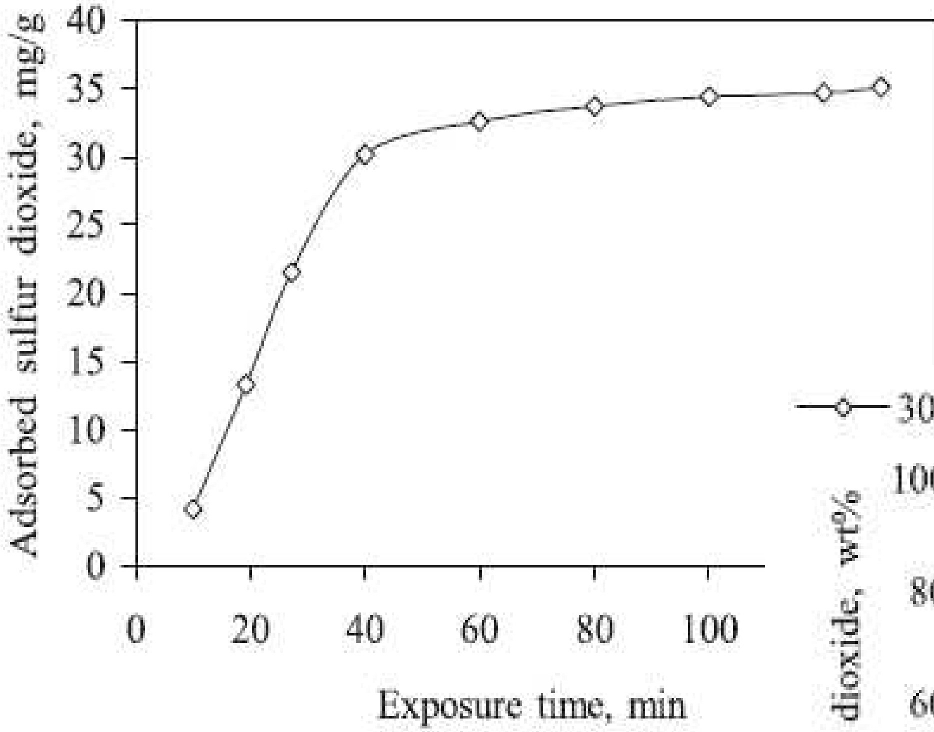
Catalytic Oxidation of SO_2 on Zeolites

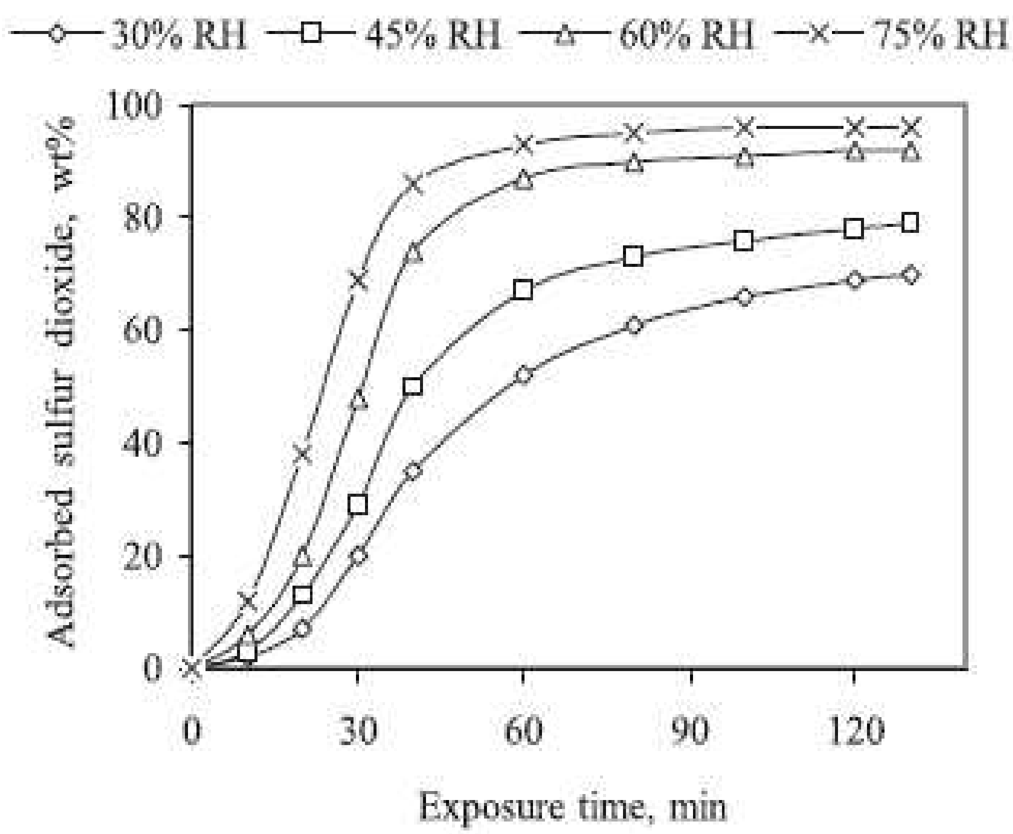
- SO_2 weakly adsorbs to powdered zeolite in the presence of water vapor. Will release upon heating.
- The SO_2 can be oxidized to sulfate by H_2O_2, making H_2SO_4.
- Disadvantage: adsorbed CO_2 must be washed off with HCl, then D.I. water.
- Adsorption range: 35-72 mg SO_2/g zeolite from 290 to 350 K

Energy Sources, Part A, 28:1329–1335, 2(

Experimental Setup







Energy Sources, Part A, 28:1329–1335, 2(

SO_2 Removal

- 90% to 98% using wet scrubbers
- Up to 80% using dry scrubbers
- Limited to SO_2 at 2000 ppm

Table 1b: Summary of Cost Information in $/MW (2001 Dollars) [a]

Scrubber Type	Unit Size (MW)	Capital Cost ($/kW)	O&M Cost [b] ($/kW)	Annual Cost ($/kW)	Cost per Ton of Pollutant Removed ($/ton)
Wet	> 400	100 - 250	2 - 8	20 - 50	200 - 500
	< 400	250 - 1,500	8 - 20	50 - 200	500 - 5,000
Spray Dry	> 200	40 - 150	4 - 10	20 -50	150 - 300
	< 200	150 - 1,500	10 - 300	50 - 500	500 - 4,000

[a] (EIA, 2002; EPA, 2000; Srivastava, 2001)

[b] Assumes capacity factor > 80%

EPA Flue Gas Desulfurization Fact Sheet http://www.epa.gov/ttn/catc/dir1/ffdg.pdf

Advantages/Disadvantages

- Very high pollutant removal rate
- Easily obtained reagents
- Can be built without major retrofit
- High capital and running costs
- Messy
- High disposal costs

Hg

Mercury: The Next Big Step

- US EPA estimate: 45 t Hg emissions/year from coal electric plants.
- Average of 0.1 mg Hg/ton coal
- 60% of all Hg in coal is released to atmosphere
- Other pollution control devices can also capture mercury.
- Different installed control techs and conditions mean each plant must develop its own plan.

J. Air & Waste Manage. Assoc. **53**:1318-1325

Current Hg Testing

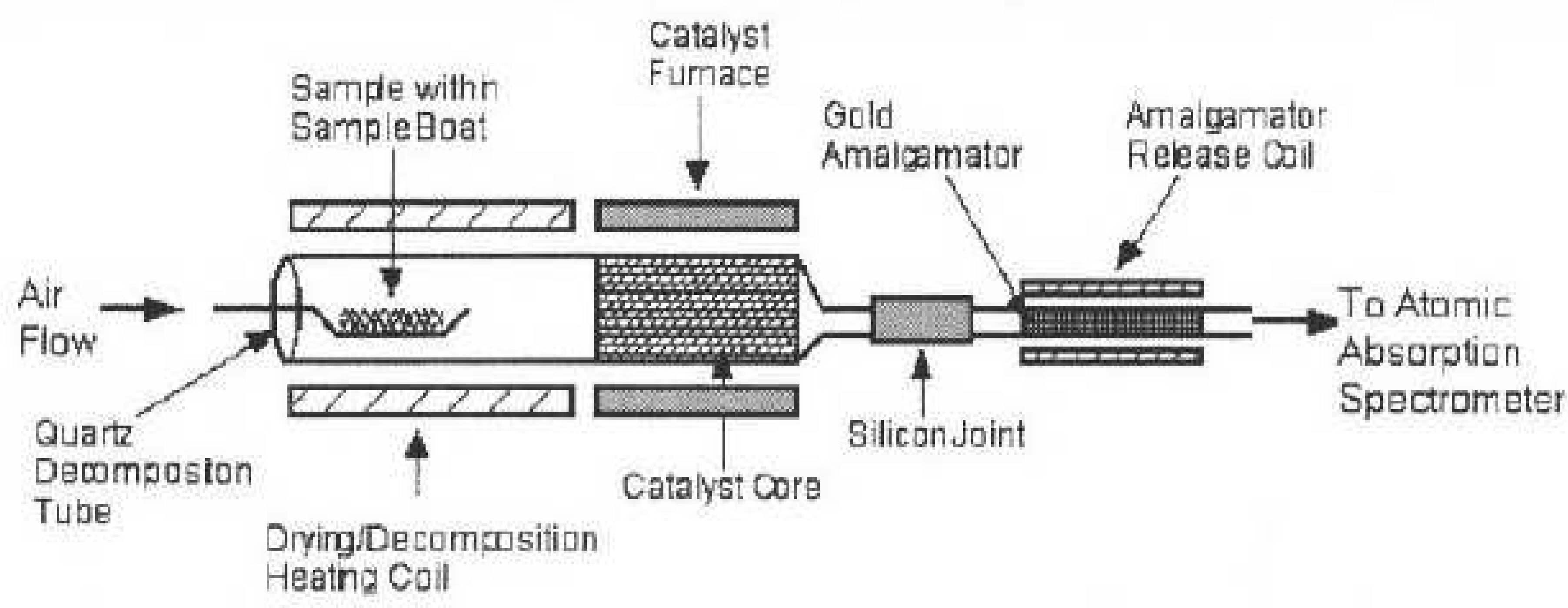
- In coal: oxygen bomb/AA spectroscopy
  - ASTM D-3684 (up to 30% SD)
- In stack gases (direct measurement):
  - EPA 29, EPA 101A, Ontario Hydro Method, MESA
- Measurements are limited, difficult, long, and expensive.
- Continuous emissions monitoring (CEM):
  - Still in development, need validation, problems with interfering species.

EPA Method 7473

- Thermal decomposition, amagalmation, and AA spectroscopic analysis
- Normally used for water/soil.
- All solid byproducts of fuel burning and pollution controls can be measured.
- Use partial mass balance to calculate Hg emitted.
- 5 min/sample
- No sample prep.

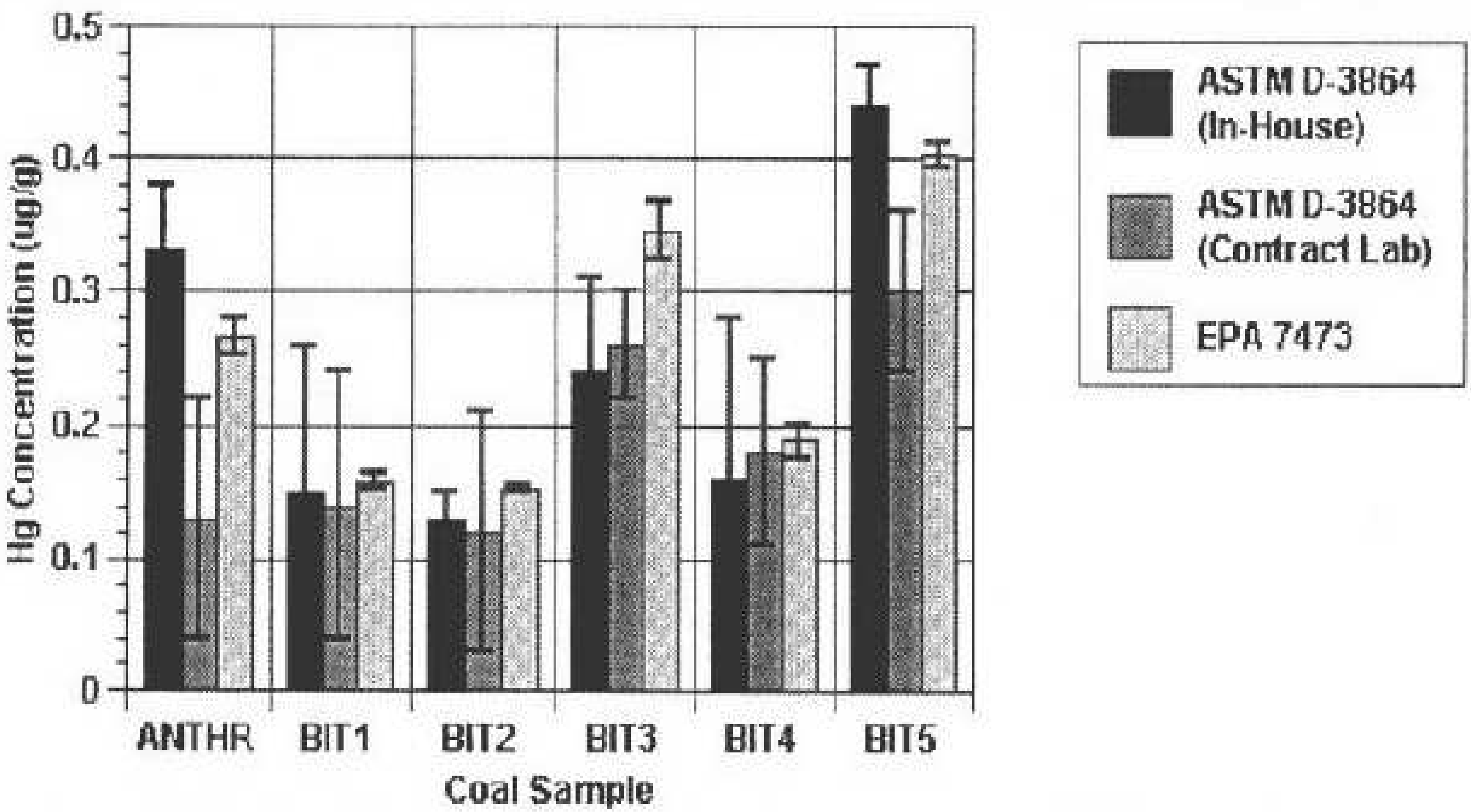
Boylan, H.; R. Cain; H. M. Kingston. *J. Air & Waste Manage. Assoc.* **53**:1318-1325

Direct Mercury Analyzer
Milestone, Inc.



Boylan, H.; R. Cain; H. M. Kingston. *J. Air & Waste Manage. Assoc.* **53**:1318-1325

Validation of EPA 7473 with Coal



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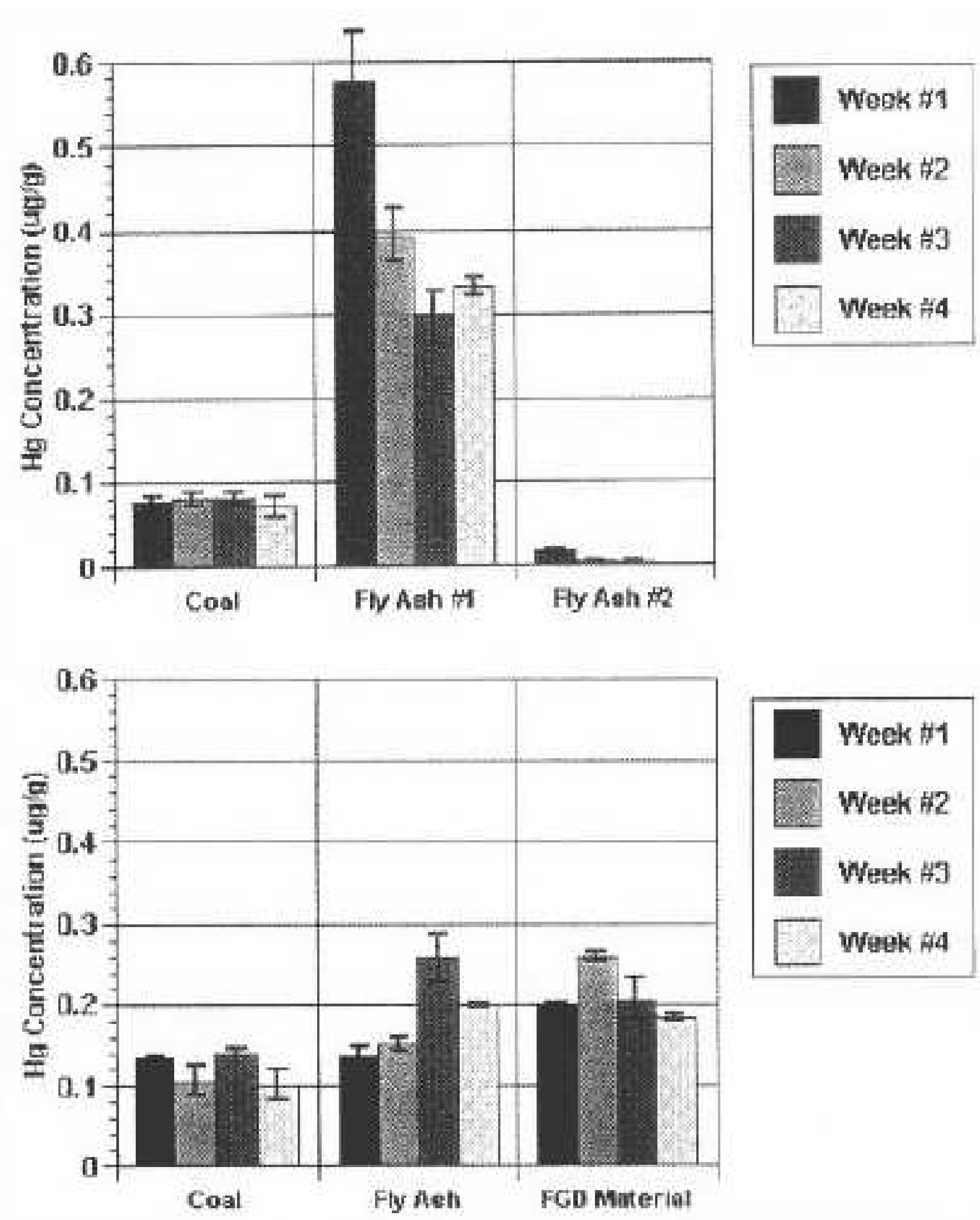

Low NO_x Burner

----- vs. -----

Conventional Burner

Boylan, H.; R. Cain; H. M. Kingston.
J. Air & Waste Manage. Assoc.
53:1318-1325

Hg Emission by Control Device

	Hg captured by sink	Hg emitted
FGD	68% on FGD material	11% (11 kg/year)
Low NO_x burner and ESP	43% on fly ash	57% (51 kg/year)
ESP only	1% on fly ash	99% (88 kg/year)

Boylan, H.; R. Cain; H. M. Kingston. *J. Air & Waste Manage. Assoc.* **53**:1318-1325

Mercury

- Chlorine present in coal will oxidize the mercury to Hg^{2+}
- Oxidized mercury can be removed more easily by scrubbers than elemental mercury
- Hg^{2+} is much more soluble in water than Hg^0

Chen, L. Fuel. **86**: 4, 603-610.

Analysis of Power Plant Hg Capture

	CNS-P1	CNS-P2	CNS-P3	CNS-P5	CNS-P6	OH-LNB	EERC1
Fuel							
S, daf wt %	4.088	4.110	4.340	4.540	3.994	4.220	4.805
Cl, daf wt %	0.128	0.174	0.135	0.156	0.151	0.091	0.0419
Hg, ppm	0.139	0.098	0.110	0.089	0.220	0.149	0.157
Boiler							
Rating, MW	290	193	180	–	1355	1338	1310
O_2, %	6.5	7.5	4.9	4.9	6.0	4.0	4.1
FGD							
Type	MgLime	LS-FO	LS-NO	LS-NO	MgLime	MgLime	LS
η_{SO2}, %	97	82	87	82	96	96	95
Slurry pH	6.5	6.1	5.8	5.8	6.5	–	–
L:G, gpm/acfm	60–75	94	73	50	30	30	–
^{IN}Hg, μg/dscm	8.2	6.5	10.6	6.8	17.9	9.1	8.2
$^{IN}f_{Hg2+}$	0.736	0.797	0.874	0.703	0.707	0.872	0.572
^{OUT}Hg, μg/dscm	3.2	2.1	1.9	2.7	7.42	3.5	5.1
$^{OUT}f_{Hg2+}$	0.159	0.124	0.150	0.382	0.162	0.370	0.198
η_{HgCl2}, %	91.6	95.0	96.9	78.4	90.5	83.7	78.5
f_{SCRB}, %	56.2	67.9	82.4	59.8	61.8	58.5	38.0

Niksa, S.; N. Fujiwara. *J. Air & Waste Manage. Assoc.* **55**:970-

Recommendations

- Using pre-scrubbers to eliminate HCl is a bad idea. Less Hg is captured.
- HCl and O_2 levels along with FGD temp are most important in capturing Hg. No other factors correlate.
- Selective catalytic reduction (SCR) in combination with wet scrubber will eliminate most Hg, but more research must be done to make sure it is predictable. (Turkey)

Niksa, S.; N. Fujiwara. *J. Air & Waste Manage. Assoc.* **55**:970–

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Byproducts

- **Slag** – contains metal oxides, phosphorous, and ash. It can be used in concretes and fertilizers.
- **CFB ash** – good for blending with construction materials (gypsum). Very basic, so OK for landfills.
- **Slurry** – difficult to move and store before drying. Contains calcium sulfate.

Green?

- Do pollution controls make fossil fuel-fired power plants green?
  - Pollution controls require large amounts of energy and reagents to run.
  - Combustor controls are better than flue gas controls.
  - Catalysts and easily recycled/cleaned asorbents should be preferred.