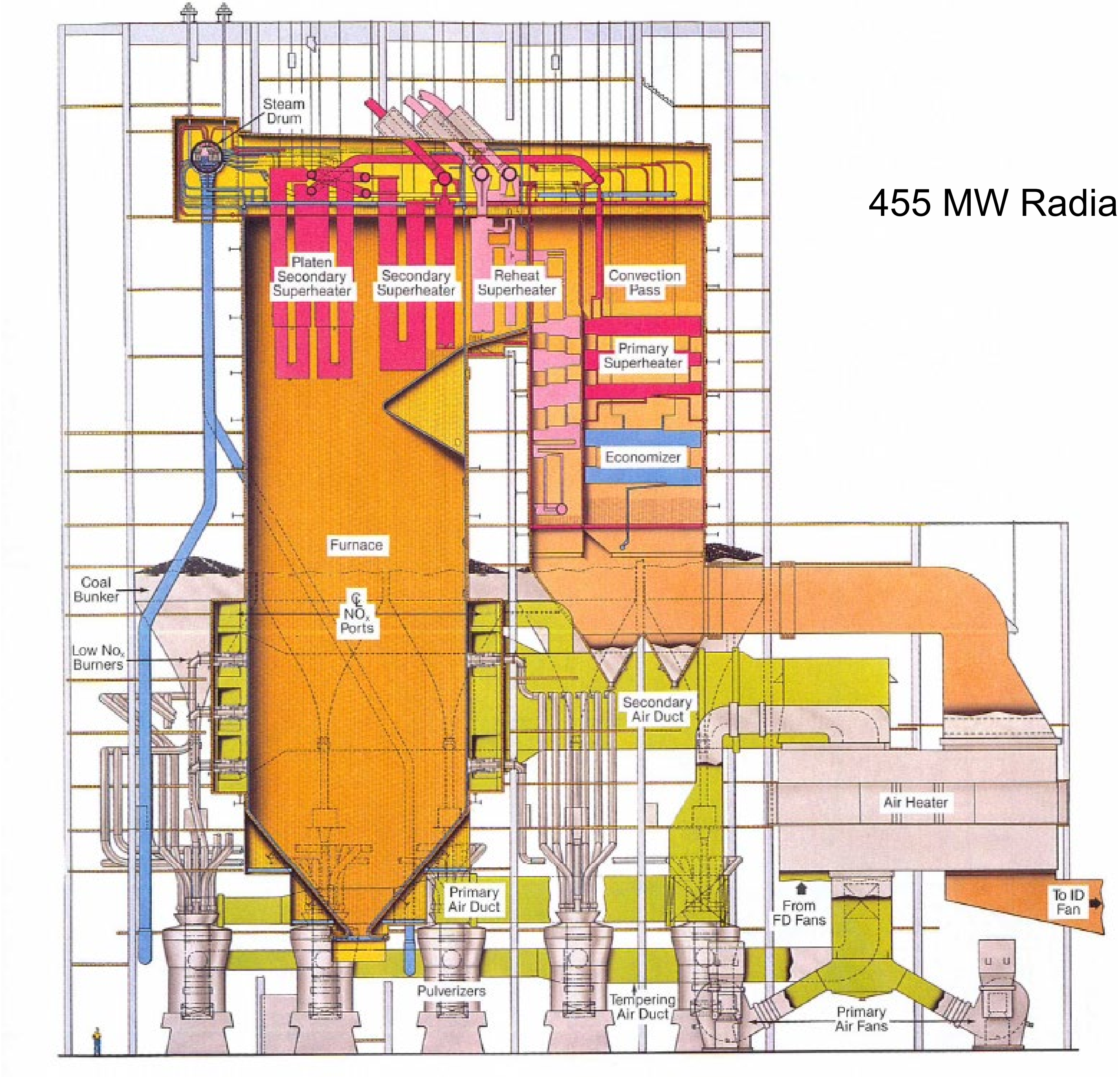
Class 14

Mineral Matter Transformations and Deposition

455 MW Radiant Boiler



From Steam, by Babcock & Wilcox

Question 1

- Discuss some of the different physical mechanisms that result in deposition of mineral matter on furnace walls and boiler tubes. Also, please discuss the influence of particle size (in relative terms) on each mechanism.

Transport Mechanisms

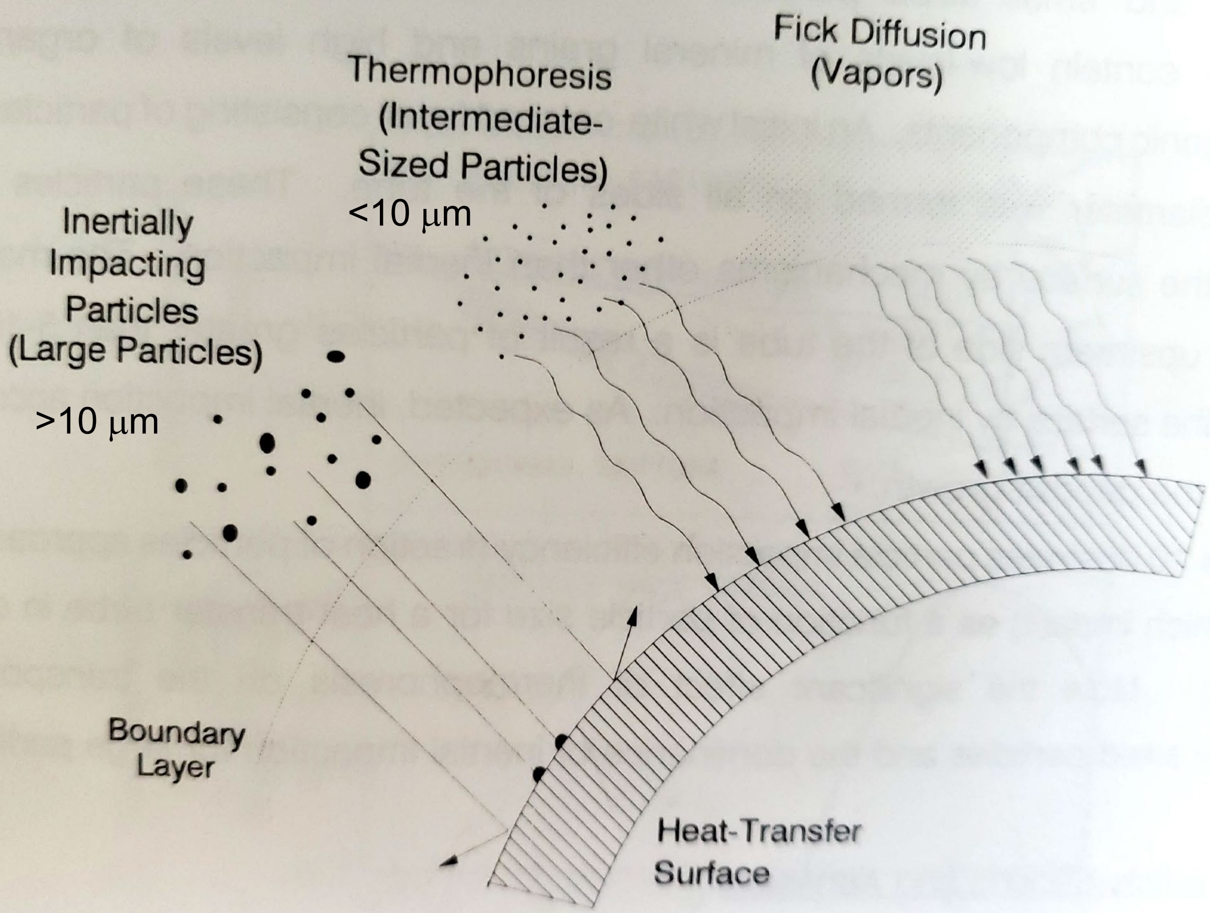


Fig. 4.8 Ash transport mechanisms to heat-transfer surfaces.

Low Temperature Fouling

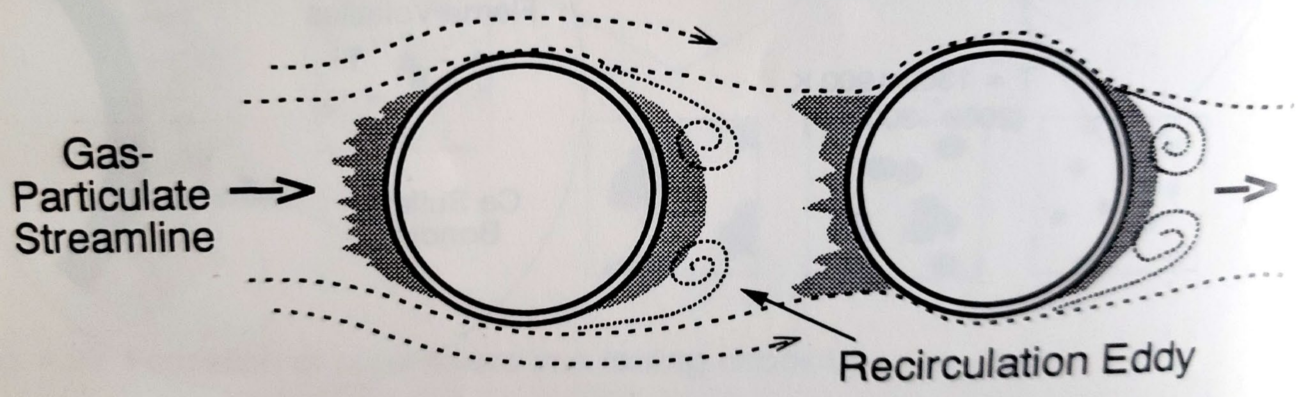


Fig. 4.23 Low-temperature fouling deposits.

Deposits on Tube

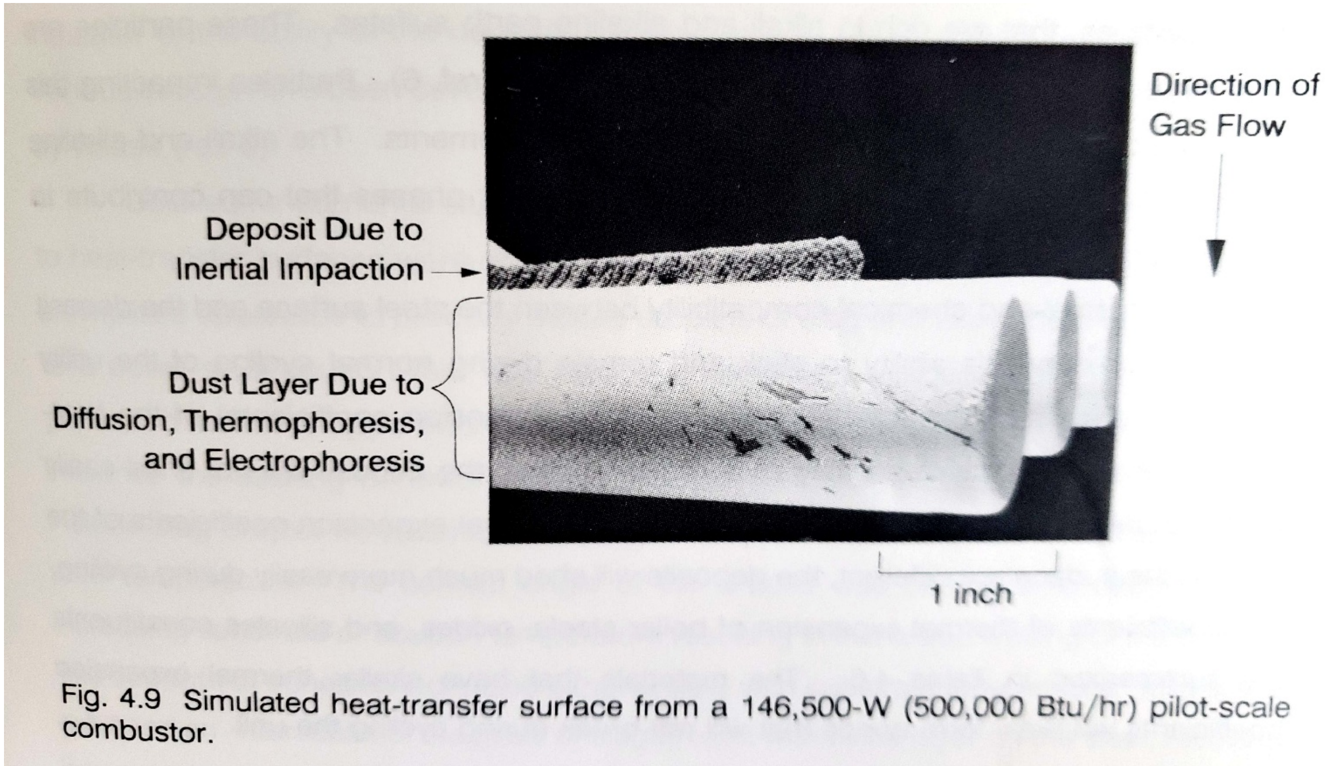


Fig. 4.9 Simulated heat-transfer surface from a 146,500-W (500,000 Btu/hr) pilot-scale combustor.

Diameter Dependence

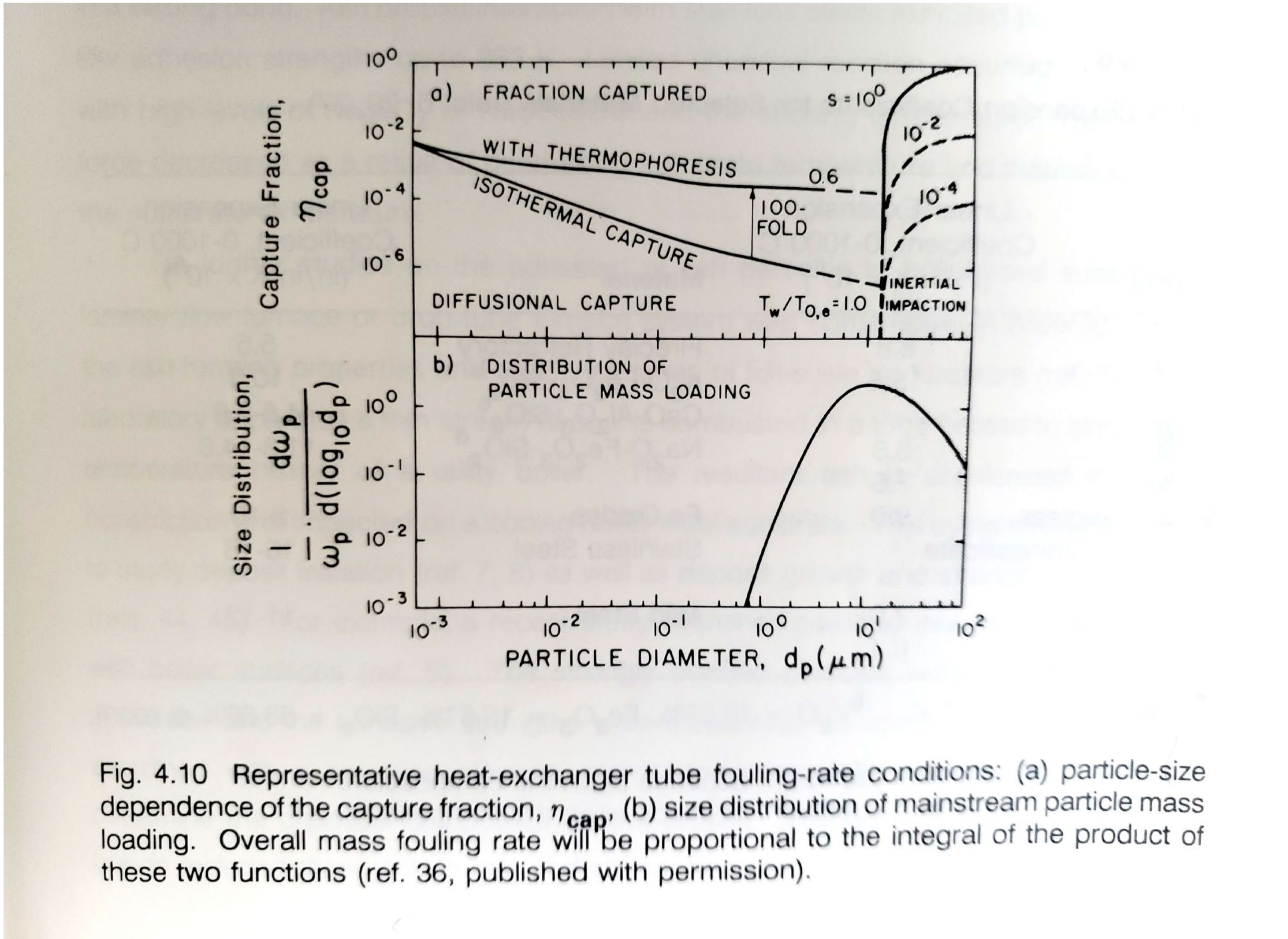


Fig. 4.10 Representative heat-exchanger tube fouling-rate conditions: (a) particle-size dependence of the capture fraction, η_{cap}, (b) size distribution of mainstream particle mass loading. Overall mass fouling rate will be proportional to the integral of the product of these two functions (ref. 36, published with permission).

Summary of Convective Pass Deposits

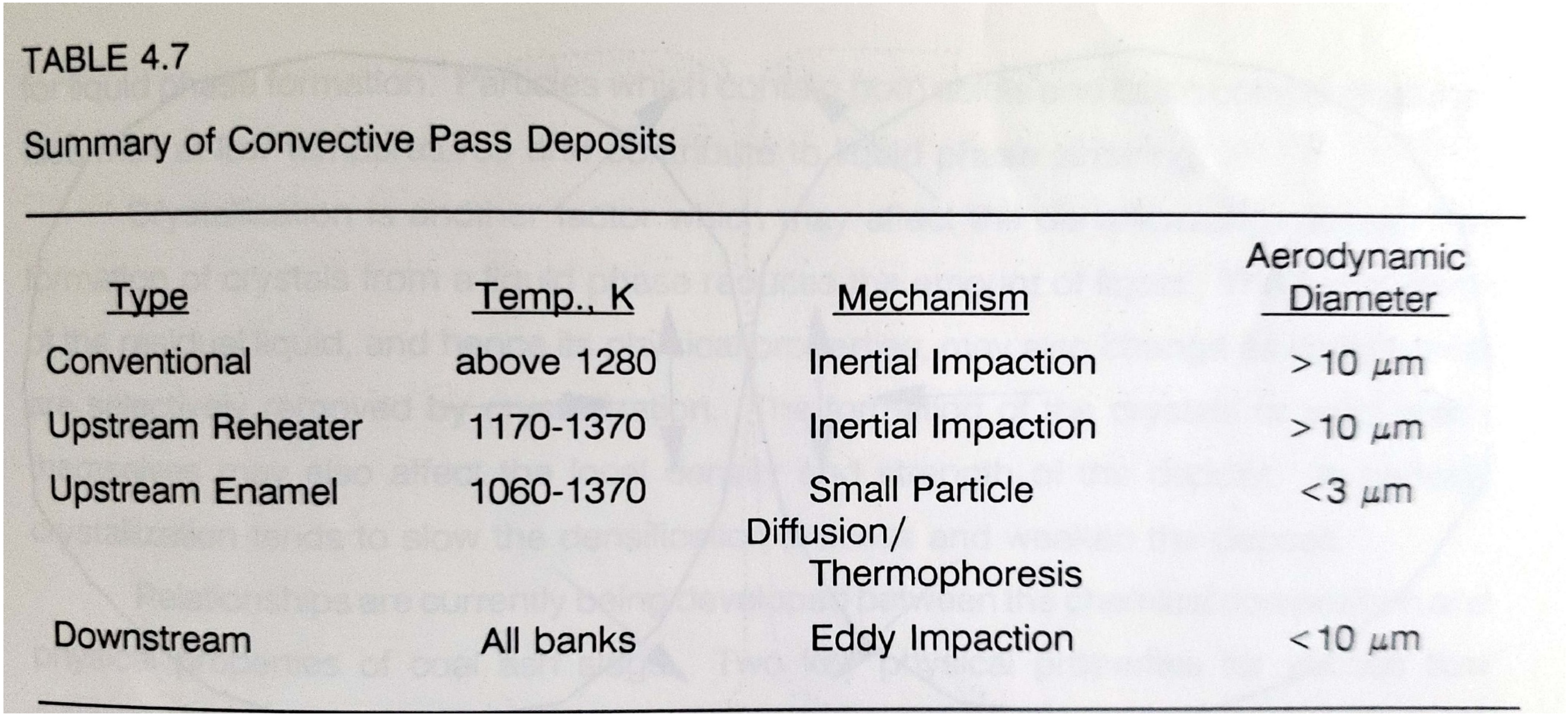


TABLE 4.7

Summary of Convective Pass Deposits

Type	Temp., K	Mechanism	Aerodynamic Diameter
Conventional	above 1280	Inertial Impaction	>10 μm
Upstream Reheater	1170-1370	Inertial Impaction	>10 μm
Upstream Enamel	1060-1370	Small Particle Diffusion/ Thermophoresis	<3 μm
Downstream	All banks	Eddy Impaction	<10 μm

2. Slagging vs. Fouling

(Slagging is in radiant section, Fouling is not)

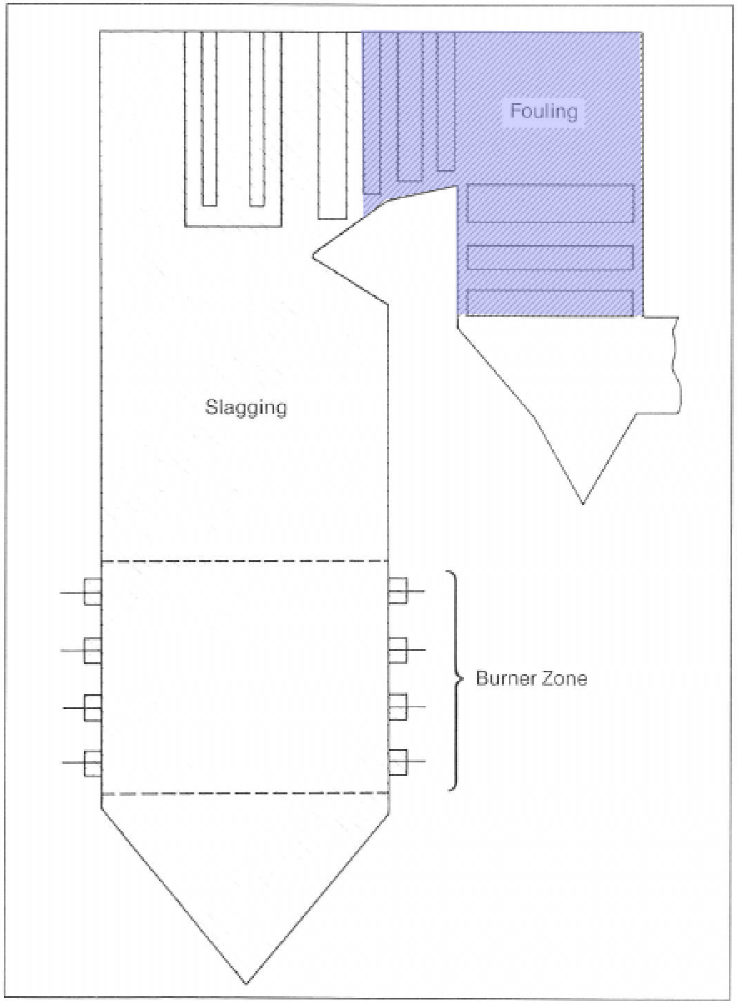


Fig. 2 Deposition zones in a coal-fired boiler.

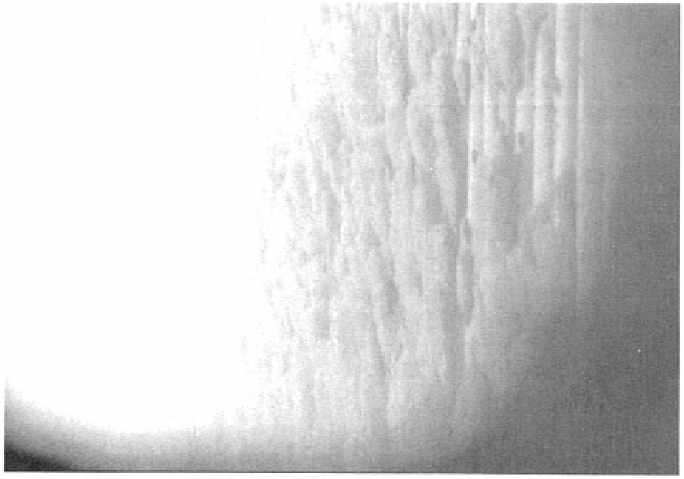


Fig. 3 Heavily slagged surface.

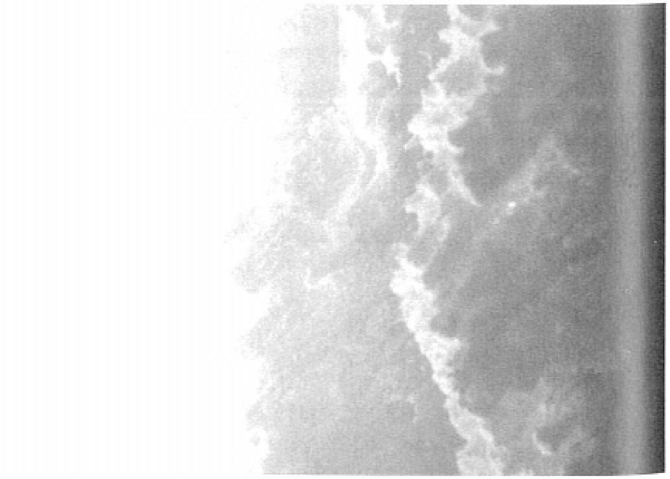


Fig. 4 Heavily fouled surface.

From STEAM by Babcock & Wilcox

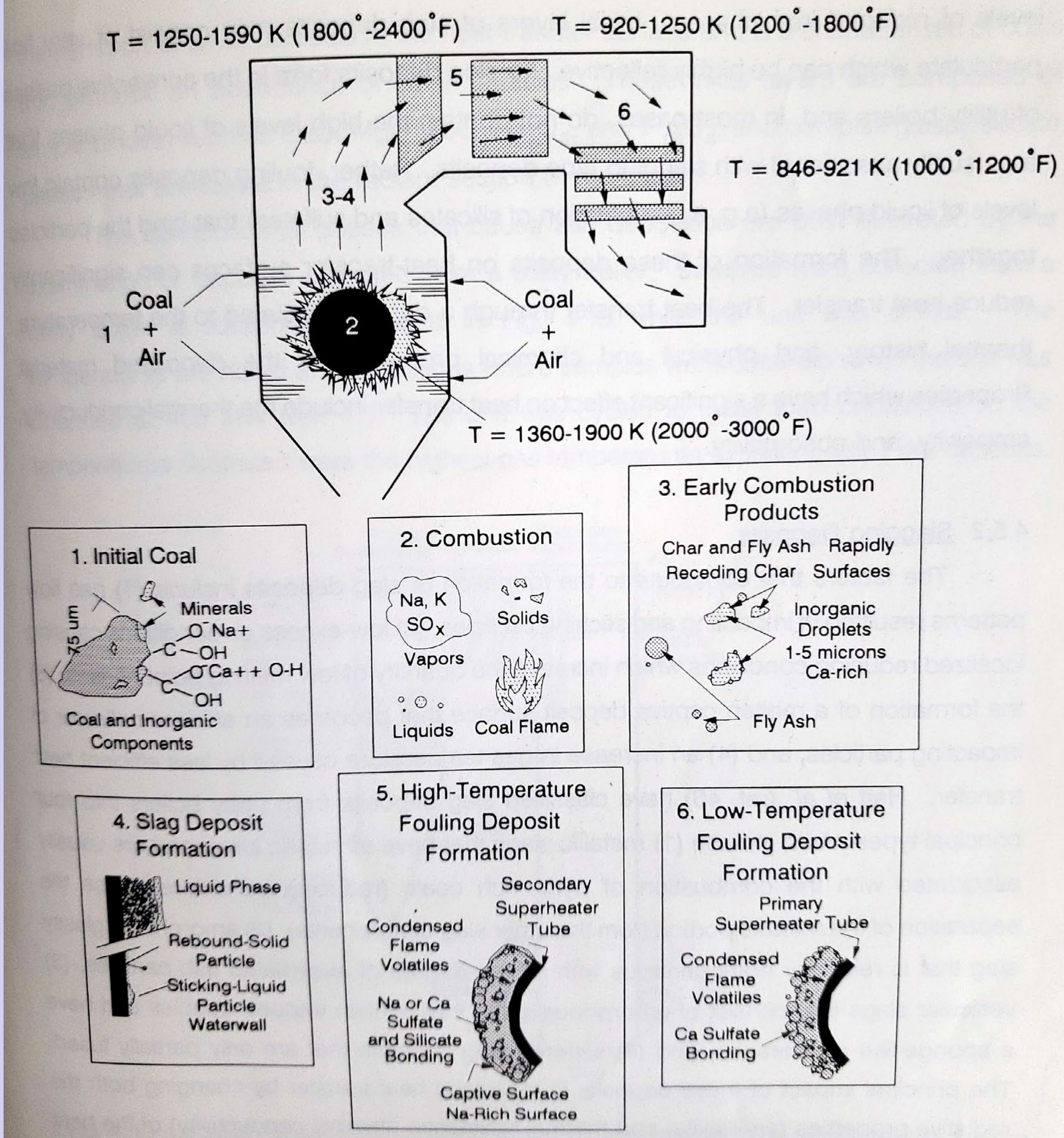


Fig. 4.12 Ash deposition phenomena in utility boilers.

Another View of Pathways

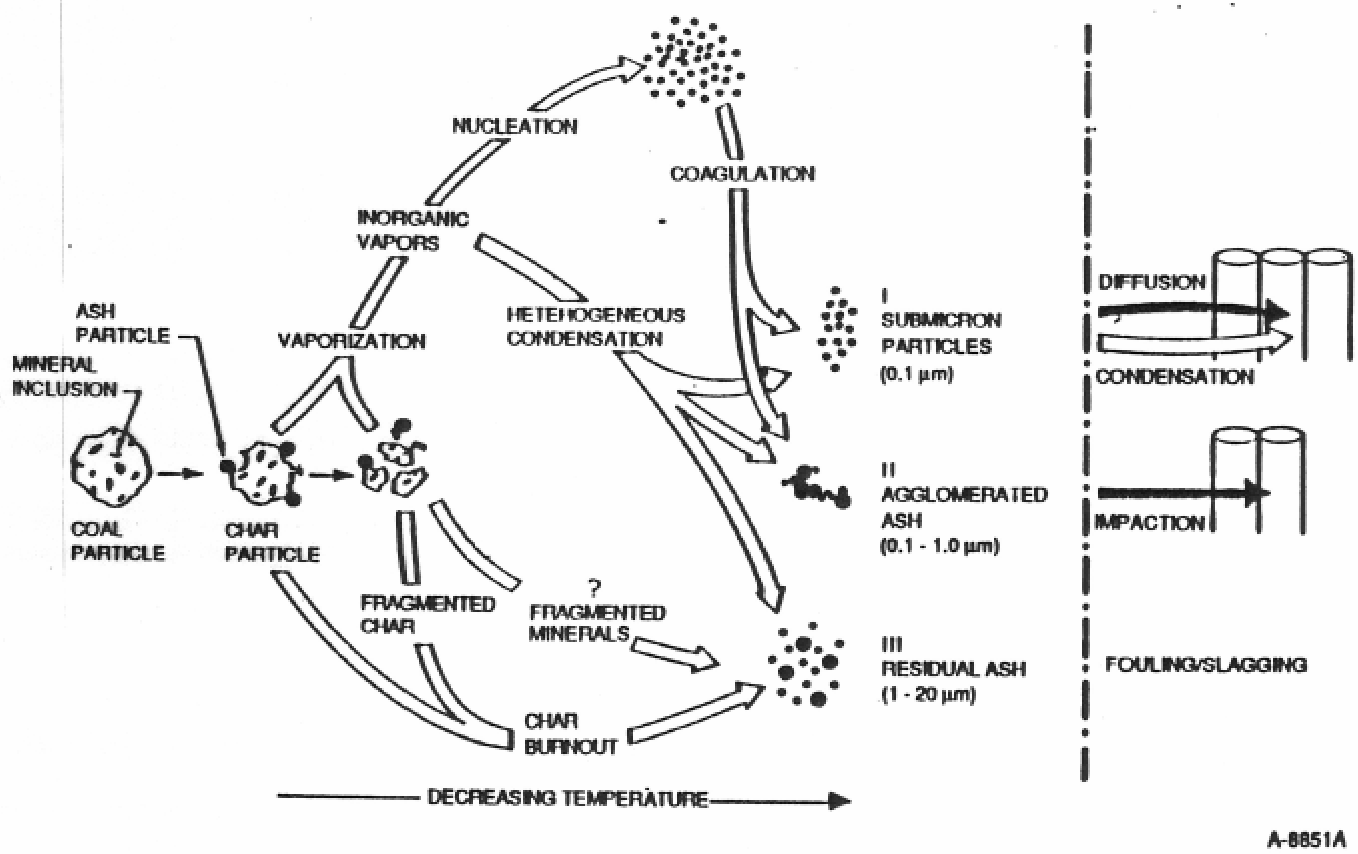


Figure 1. Hypothesis - flyash formation processes.

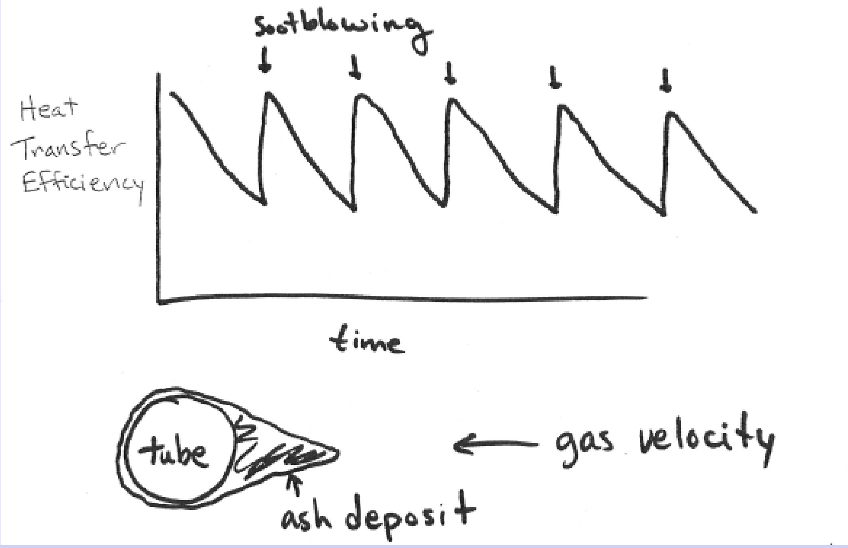
from PSI Technology Company

Physical Transformations of Inorganics

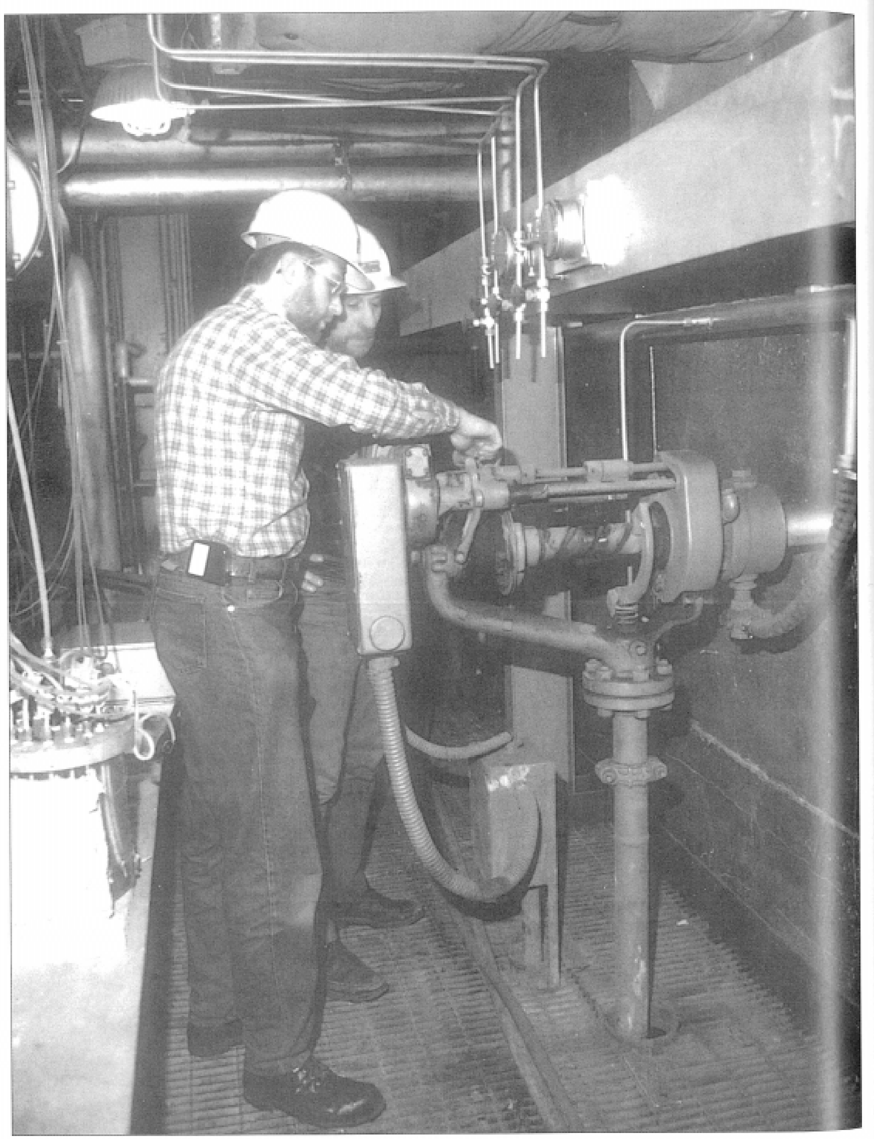
1. Coalescence of individual mineral grains within char particle
2. Shedding of ash particles
3. Incomplete coalescence due to disintegration of the char
4. Convective transport of ash from the char surface during devolatilization
5. Fragmentation of inorganic mineral particles
6. Formation of cenospheres
7. Vaporization and subsequent condensation of inorganic components upon gas cooling

Assignment: Please draw one of these on the board

3. Sootblowing



- Blow in air or steam to remove ash deposits (not soot)
- Performed routinely in cyclic manner
- Frequency of sootblowing must be short enough to prevent fusing of deposit
  - Deposit surface temperature increases with increasing deposit thickness



Wall sootblower inspection.

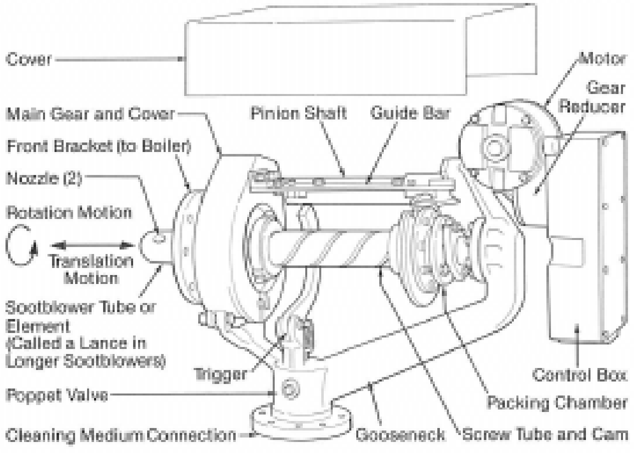


Fig. 1 Model IR wall blower.

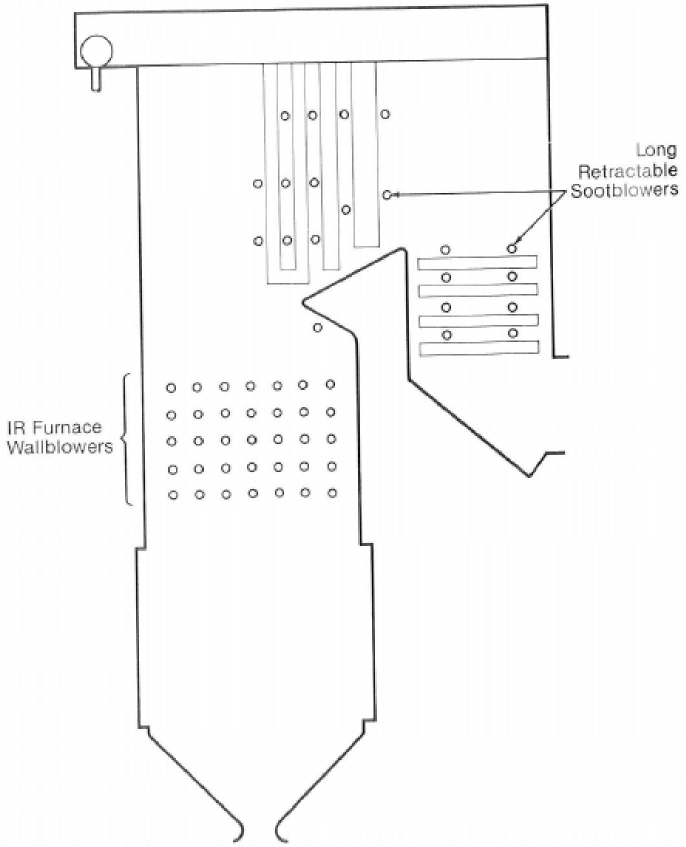


Fig. 5 Typical sootblower locations in a large coal-fired boiler.

Figures from STEAM by Babcock & Wilcox

4. How can deposition affect heat transfer in the furnace?

- Insulates walls
  - Lower thermal conductivity
- Lowers emissivity of walls
  - Lower radiant flux
- Fouling blocks convective passages
  - Lower convective flux
- Corrosion
  - Down time!

5. Why would the deposit on the upstream surface of a steam tube be different than the deposit on the downstream side?

- Different size of particles

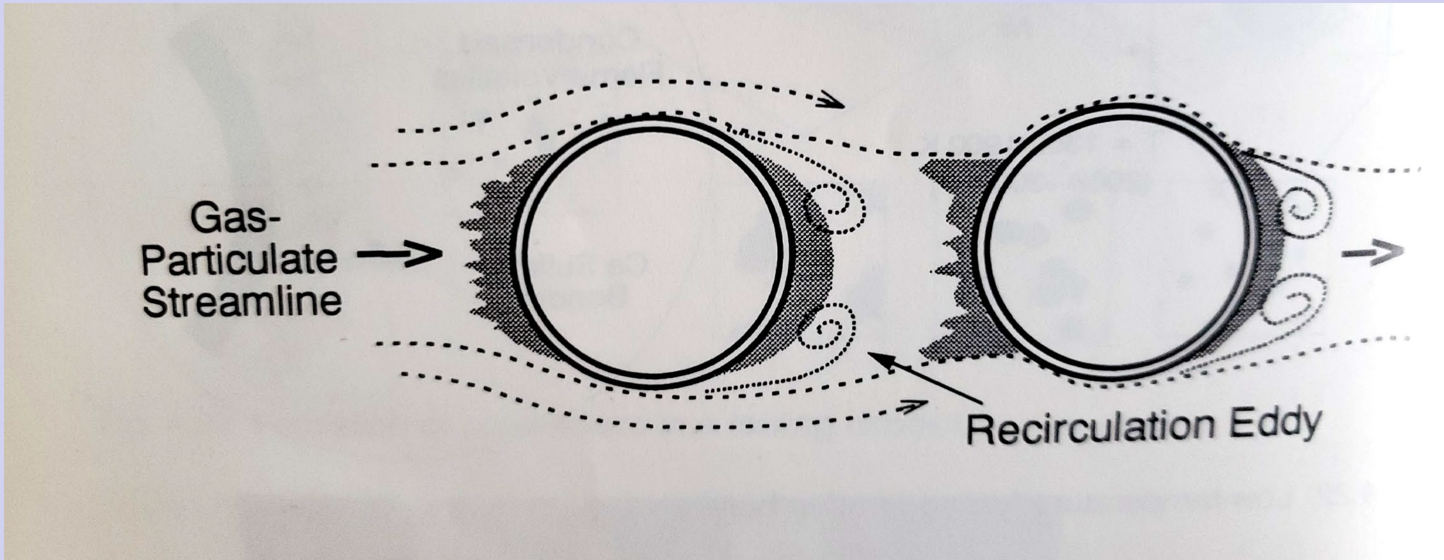


Fig. 4.23 Low-temperature fouling deposits.

Large particles impact on front side
Small particles follow eddy around to back side, entraining small particles

6. Factors that affect deposit strength

- Properties of ash deposits
  - Flyash chemistry
  - Flyash physical properties
  - Condensing constituents/ash surface properties
- Heat transfer surface properties
  - Tube temperature
  - Material (Stainless, Ferritic/ level of oxidation)
  - Surface roughness
- Reactions within deposit
  - Deposit temperature/Radiant & convective flux
  - Thermal gradient in deposit
  - Local gas T and composition
  - Residence time (seasoning)
- Primary bonding mechanisms
  - High T (> 2200°F) Silicate matrix
  - Low T (< 1800°F) Sulfate matrix

7. Deposition problems when co-firing biomass with coal

- **Extra fouling**
  - S from coal
  - Ca, Na from biomass
  - $CaSO_4$ forms between convective pass tubes
- **Extra corrosion**
  - K and Cl from biomass
- **Convective pass T too high for biomass ash**
  - Sticky deposits from lower melting ash from biomass

Slagging Deposits

- High concentrations of Fe & Si
- Generally have a large amount of liquid phase
- More prevalent with Eastern US coals
  - Abundant pyrite
  - Smaller furnaces
- Contributing factors
  - Gas flow patterns resulting in particle impaction
  - Localized reducing conditions (sticky particles)
  - A molten captive surface

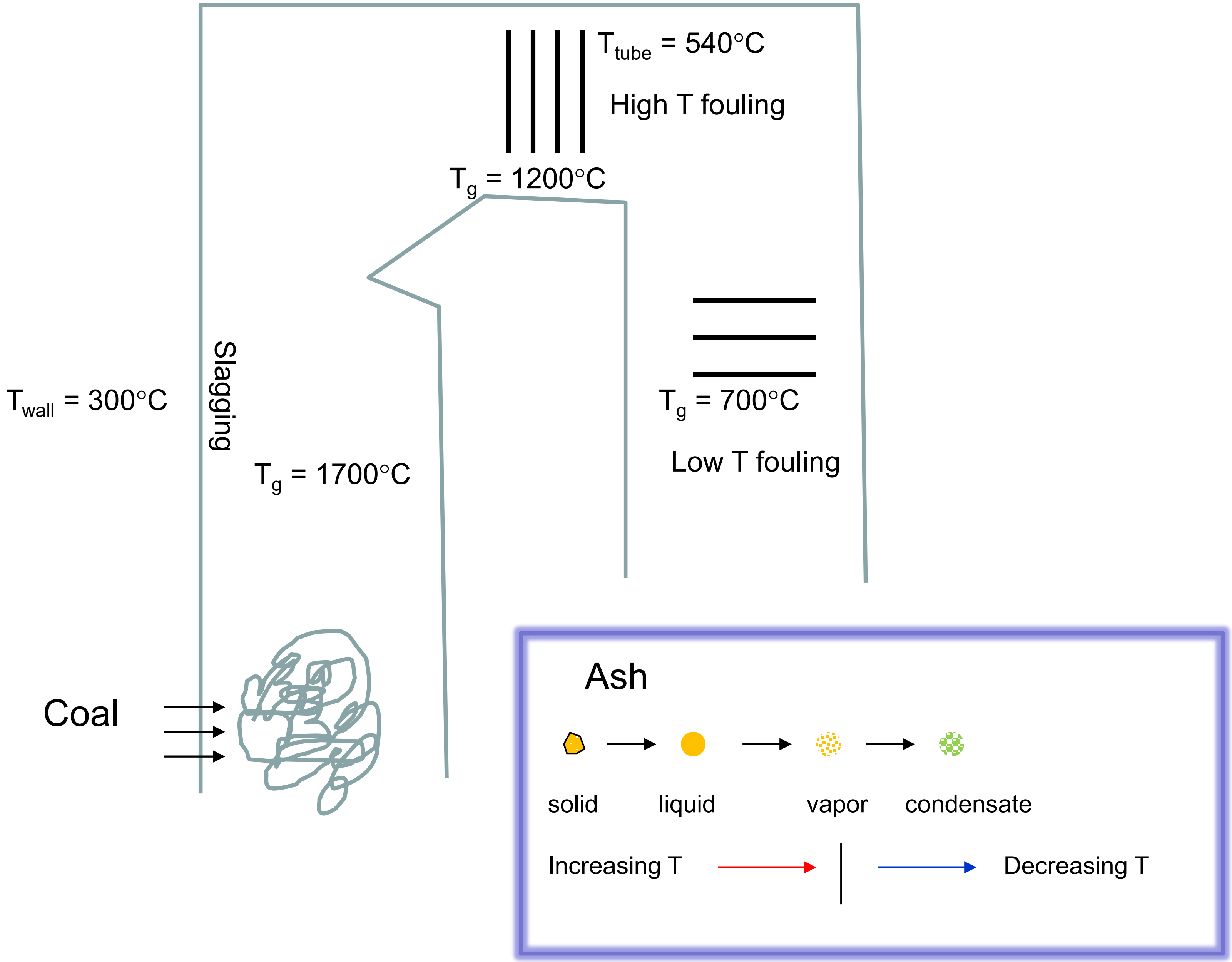
High T Fouling Deposits

- 1800-2400°F (980-1300°C)
- Occurs in the front of the convective pass
- High concentrations of Na, some Ca
- Silicate-based liquids cause strong bonding
- Layered deposits observed
- Deposit strength increases with time

Low T Fouling Deposits

- 1200-1600°F (650-875°C)
- Occurs in the reheater section
- High levels of Ca
- Sulfate-based bonding
- Silicates remain unreacted

Effect of Temperature on Deposition



T_{tube} = 540°C

High T fouling

T_g = 1200°C

T_{wall} = 300°C

Slagging

T_g = 1700°C

T_g = 700°C

Low T fouling

Coal

Ash

⬟ → ● → ⁘ → ⁘

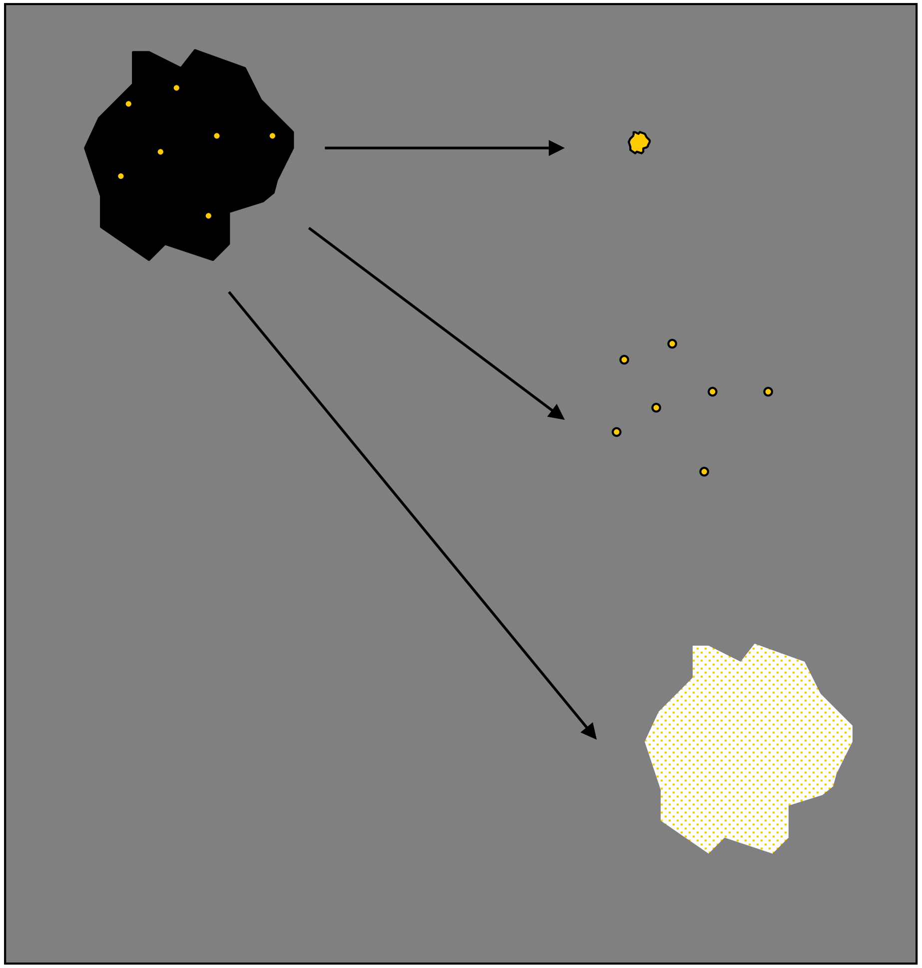
solid liquid vapor condensate

Increasing T → | → Decreasing T

Size Transformations

(Baxter’s Results)

Limiting Cases



- One “big” ash particle per coal particle
- One ash particle per mineral grain
- Complete vaporization then recondensation to fine particles
- So what really happens?

Baxter results from Sandia

- Electrically heated furnace (2-story)
- Laser-based particle size analyzer
- Detailed population balance based on changes in size distribution

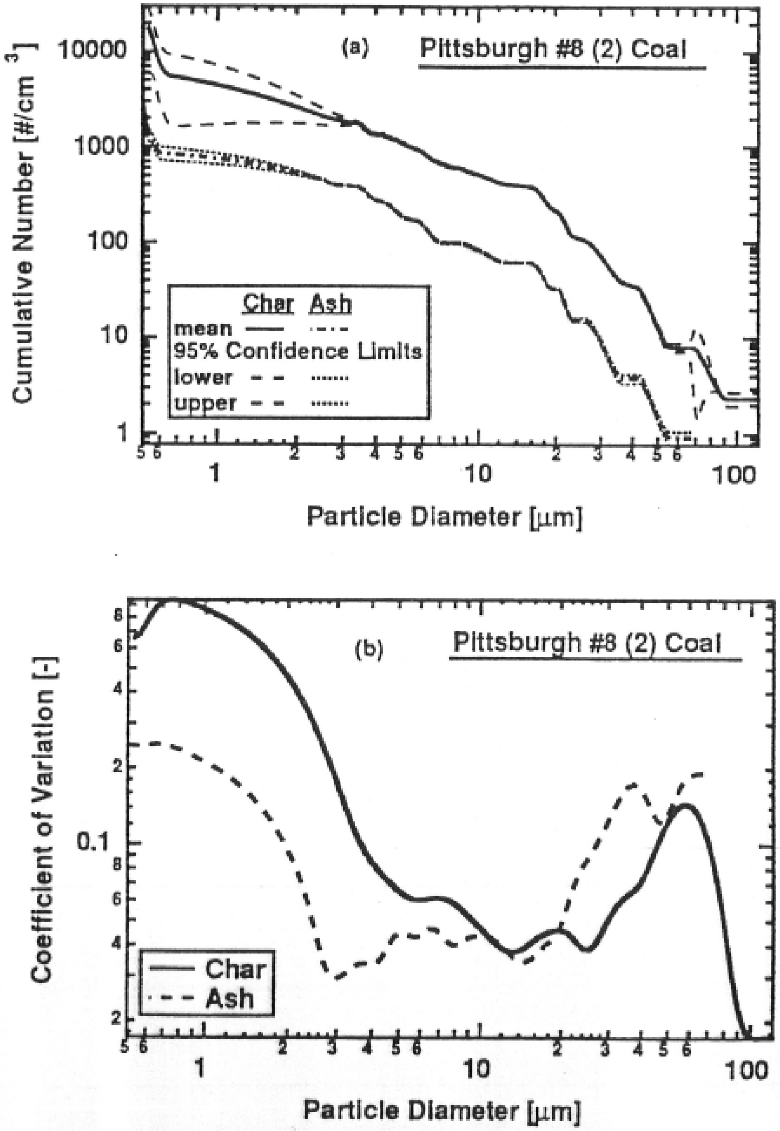


Figure 1 Cumulative particle size distributions and statistics for char and fly ash generated from the Pittsburgh #8 (2) coal.

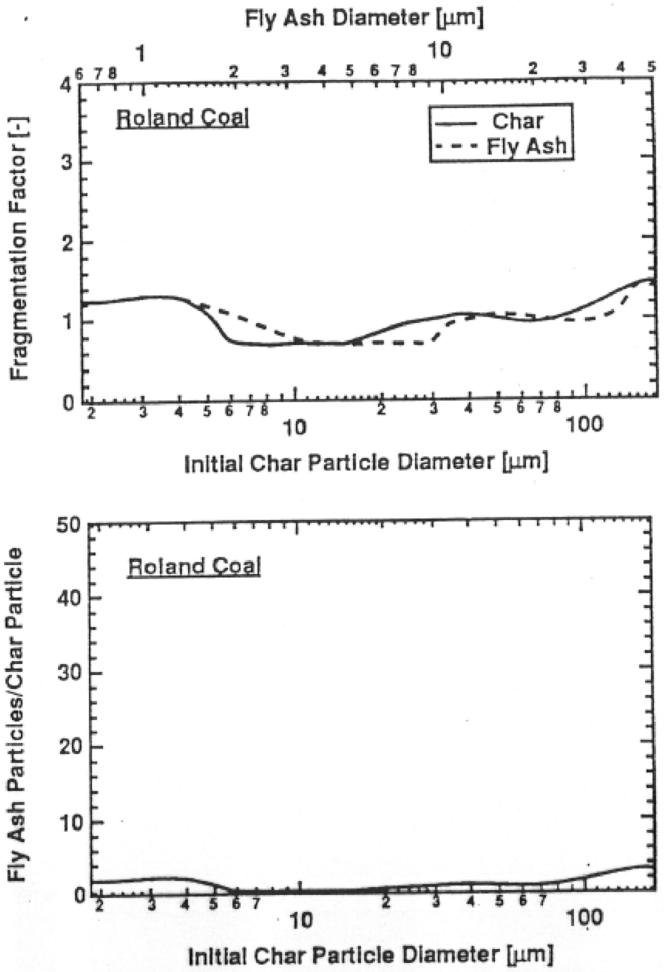
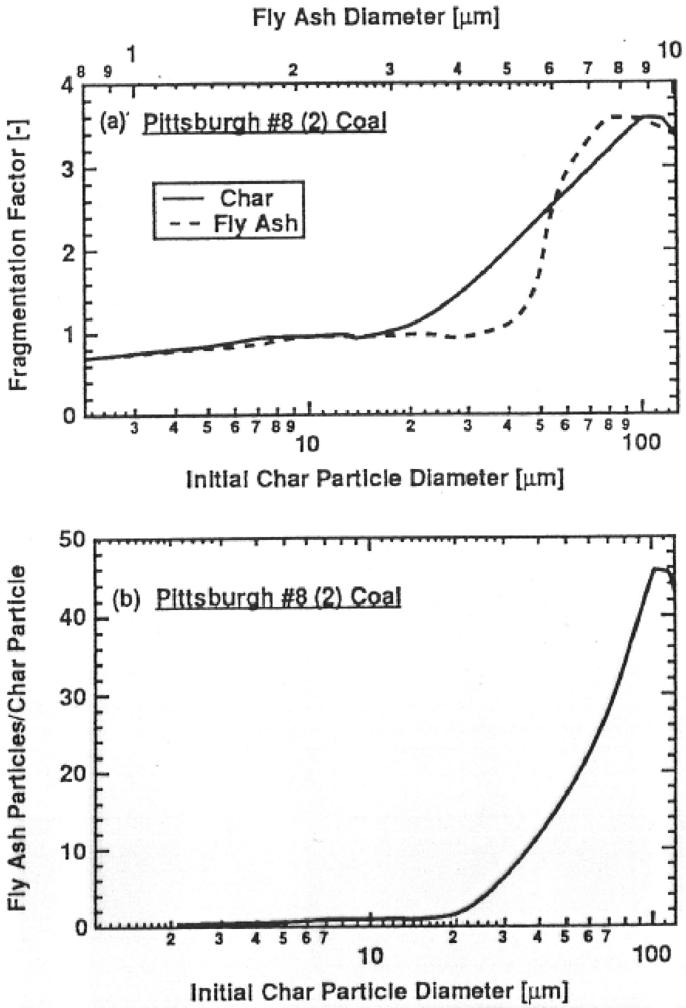


Figure 3 Variation of the fragmentation factor as a function of initial char and final fly ash particles sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a Roland-seam coal.



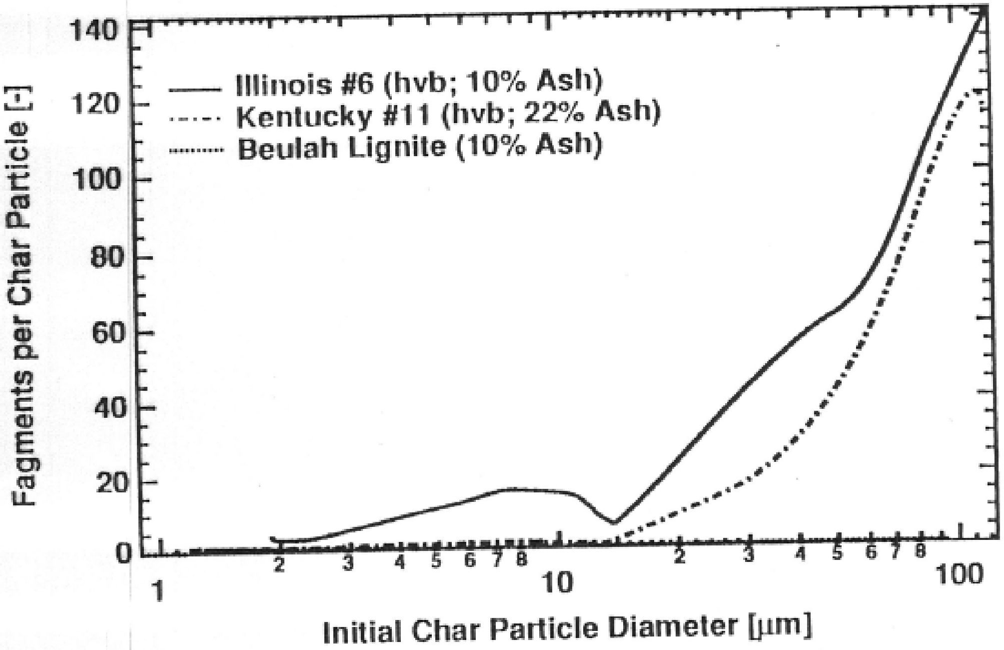


Figure 4. The number of fly ash particles formed per char particle as a function of initial char particle diameter for three additional coals.

Baxter's Fly Ash Conclusions

Fly ash formation is dependent on:

A. Particle Size

- larger particles fragment more

B. Coal Rank

- more fragments from chars that form cenospheres

C. Ash Loading

- higher ash loading allows particle to fuse together late in burnout

- Low rank coals may fragment more during devolatilization

Chemical Transformations

Difference Between Coal Ash and Flyash

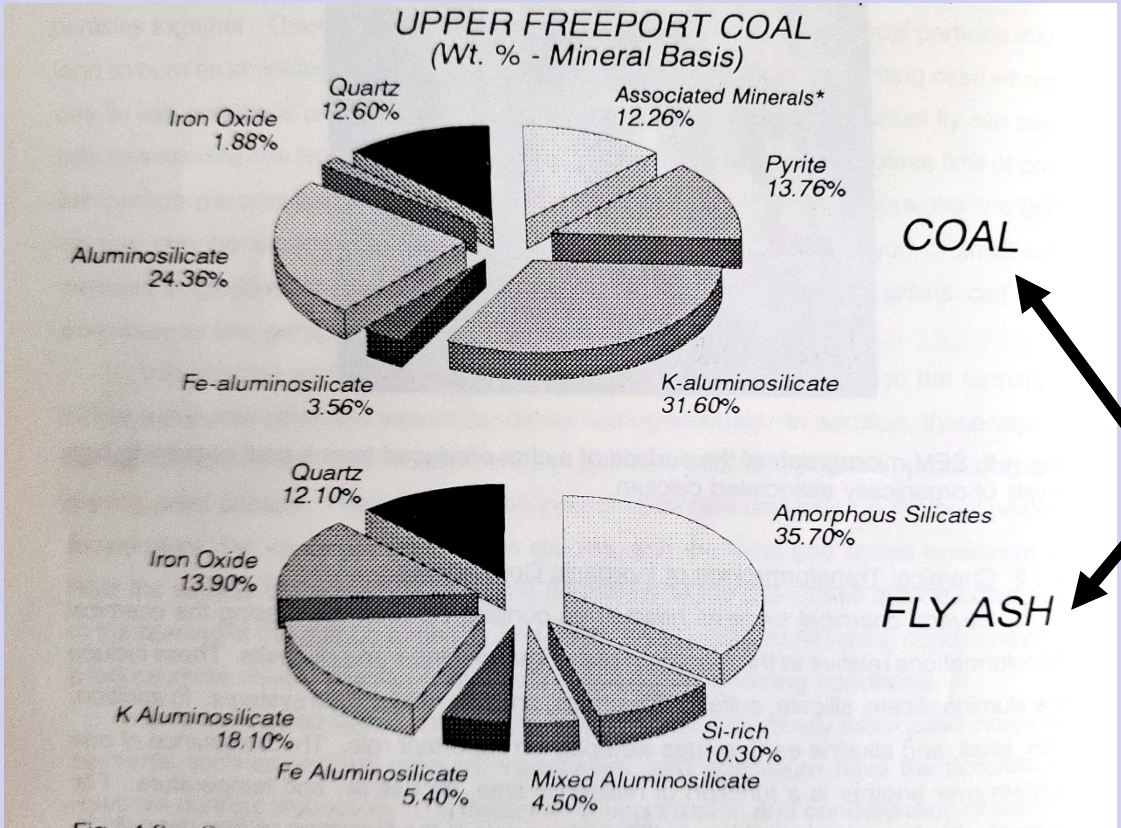


Fig. 4.6 Composition evaluation of Upper Freeport Bituminous coal ash during combustion (wt % mineral basis): (a) coal composition, (b) fly ash composition. *Mixed minerals such as quartz and pyrite.

Note change

Chemical Transformations

- Critical Chemical Systems – aluminosilicate, silicate, sulfate, phosphate, chloride, sulfide, iron, alkali and alkaline earth oxides
- Importance of each system depends on residence time, oxygen, and temperature
  - For example, iron oxides and iron sulfides play an important role in slag deposition in radiant section of furnace
- Benson et al. (1993) explains that incomplete oxidation of FeS_2 to FeS or FeO instead of to Fe_2O_3 or Fe_3O_4 can result in low melting point intermediate phases that stick to heat transfer surfaces

Alkali and Alkaline Earth Reactions

Na, K Mg, Ca

- Extremely important with respect to convective pass fouling
- Behavior of alkalies during combustion depends strongly on their form in the coal
- Carboxyl-bound alkalies or those in solution will volatilize
- Na is bound to carboxyl group in lignite and volatilizes to form NaOH
- Na also reacts with clay and quartz in vapor phase to form sodium-alumino-silicate slag droplets (lower melting point) or flyash
- NaOH also reacts with SO_2 to form $NaSO_4$
  - Low melting point (884°C)
  - Becomes part of initial sticky slag layer (fouling)

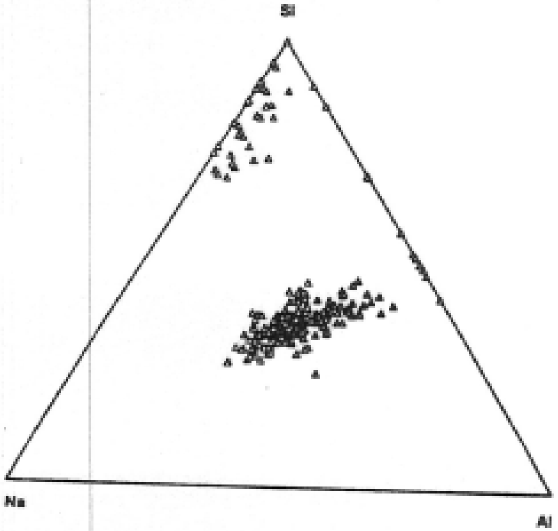
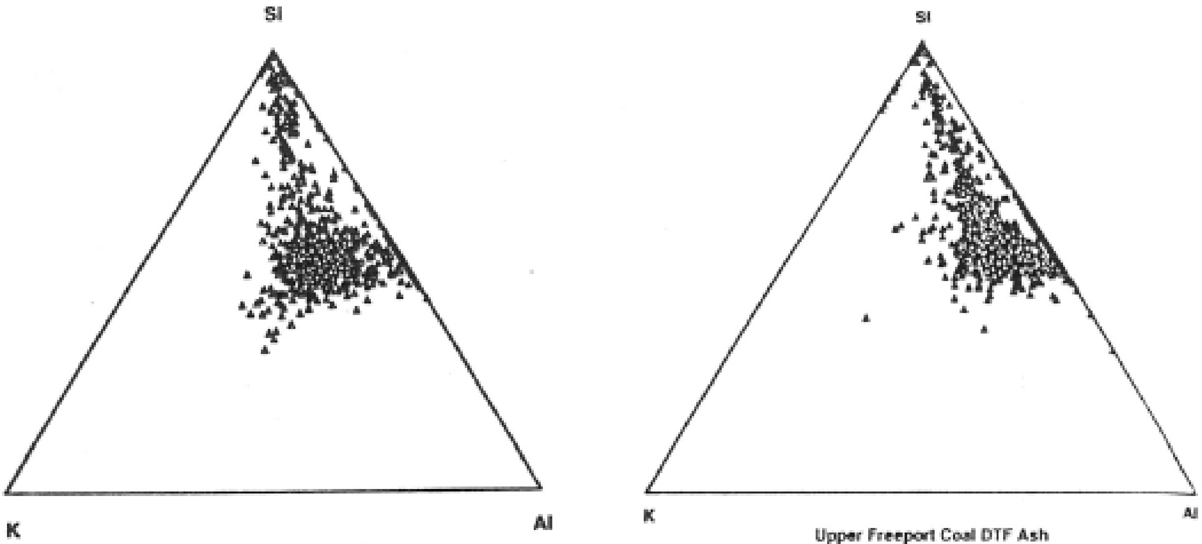


FIG. 8. Na–Si–Al diagram derived from CCSEM data for Beulah ash particles from a drop tube furnace combustion experiment.

G. P. HUFFMAN *et al.*



Upper Freeport Coal

Upper Freeport Coal DTF Ash

FIG. 7. K–Si–Al diagrams derived from CCSEM data for Upper Freeport coal and ash from a DTF experiment.

Transformation Implications to Deposition

Conclusions

1. The study of mineral matter transformations in combustion systems leads to better understanding of fouling/slagging, heat transfer, and harmful pollutant species formation.
2. Physical transformation of ash during char oxidation usually behaves between the limit of 1 ash particle per coal particle or 1 ash particle per mineral grain.
    - Swelled bituminous coal fragments readily, giving a larger particle size distribution than lignite coals
3. Different reaction mechanisms for iron, alkali and alkaline earths, and acid-base chemical groups have been suggested for several combustion regimes
4. The predictions of fouling tendencies of a certain coal can be done based on experience and based on the general trends discussed previously
5. A priori predictions are not feasible at this time due to the complex processes involved.

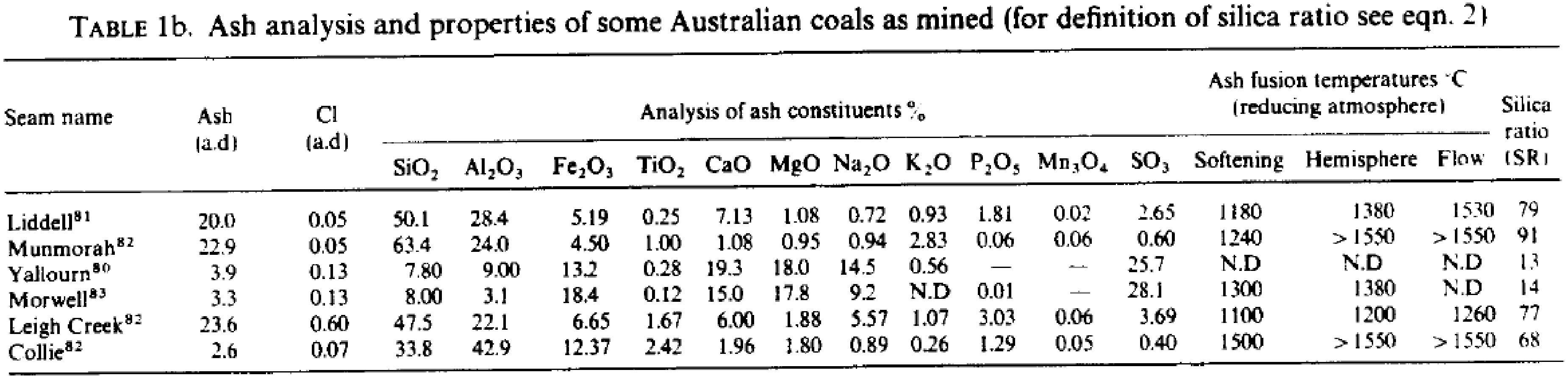


TABLE 1b. Ash analysis and properties of some Australian coals as mined (for definition of silica ratio see eqn. 2)

Seam name	Ash (a.d)	Cl (a.d)	Analysis of ash constituents %											Ash fusion temperatures °C (reducing atmosphere)			Silica ratio (SR)
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Mn_3O_4	SO_3	Softening	Hemisphere	Flow	
Liddell[81]	20.0	0.05	50.1	28.4	5.19	0.25	7.13	1.08	0.72	0.93	1.81	0.02	2.65	1180	1380	1530	79
Munmorah[82]	22.9	0.05	63.4	24.0	4.50	1.00	1.08	0.95	0.94	2.83	0.06	0.06	0.60	1240	>1550	>1550	91
Yallourn[80]	3.9	0.13	7.80	9.00	13.2	0.28	19.3	18.0	14.5	0.56	—	—	25.7	N.D	N.D	N.D	13
Morwell[83]	3.3	0.13	8.00	3.1	18.4	0.12	15.0	17.8	9.2	N.D	0.01	—	28.1	1300	1380	N.D	14
Leigh Creek[82]	23.6	0.60	47.5	22.1	6.65	1.67	6.00	1.88	5.57	1.07	3.03	0.06	3.69	1100	1200	1260	77
Collie[82]	2.6	0.07	33.8	42.9	12.37	2.42	1.96	1.80	0.89	0.26	1.29	0.05	0.40	1500	>1550	>1550	68

Wall et al. (1979) Prog. Energy Comb. Sci.

Deposition Mechanisms

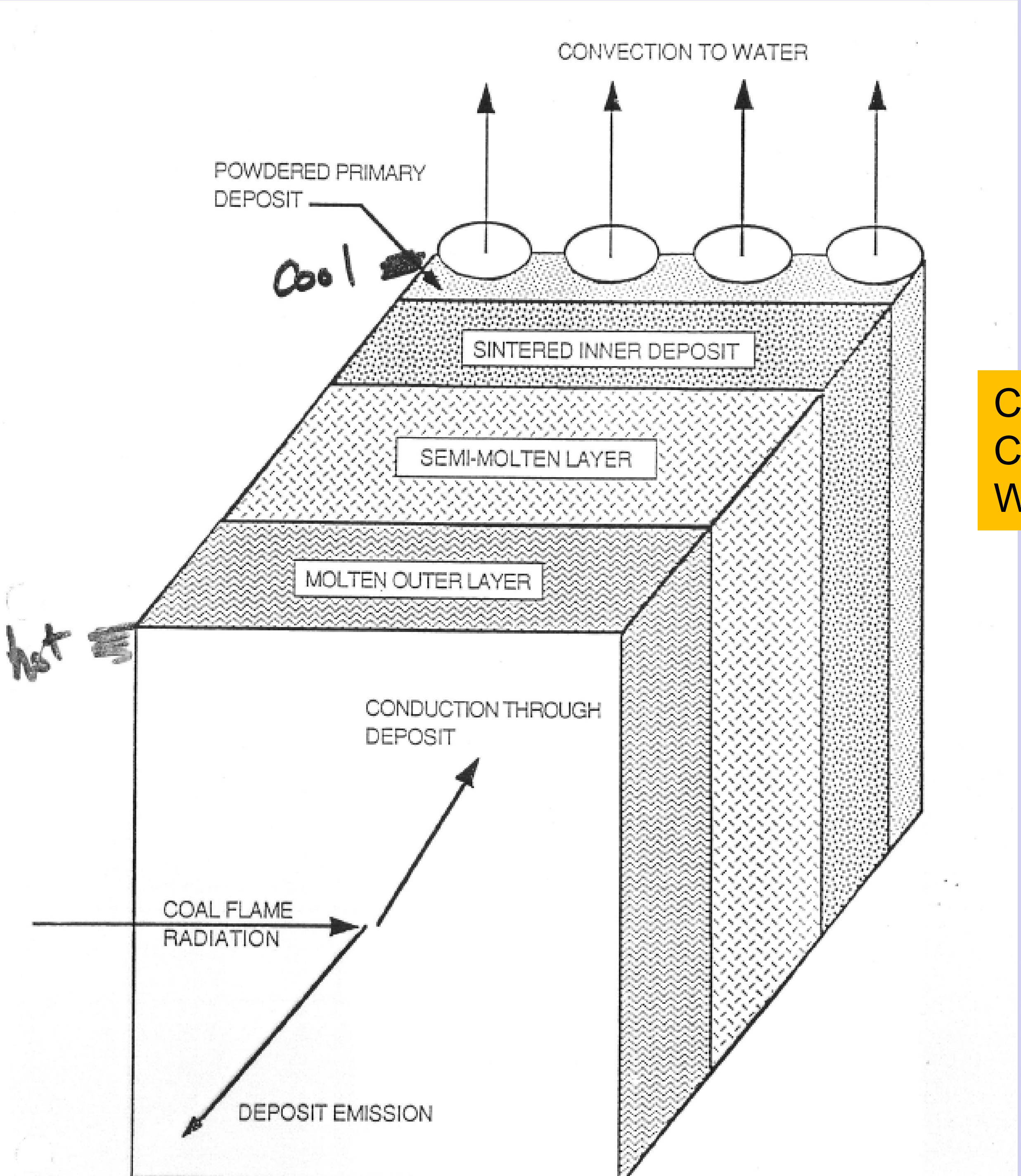
Radiant vs. Convective Conditions

Radiant Section

- Lower particle residence time
- Higher temperature
- Variable y_{O2}
- Partial coal combustion
- Pyrites and silicates play dominant role
- Vaporized minerals not as dominant

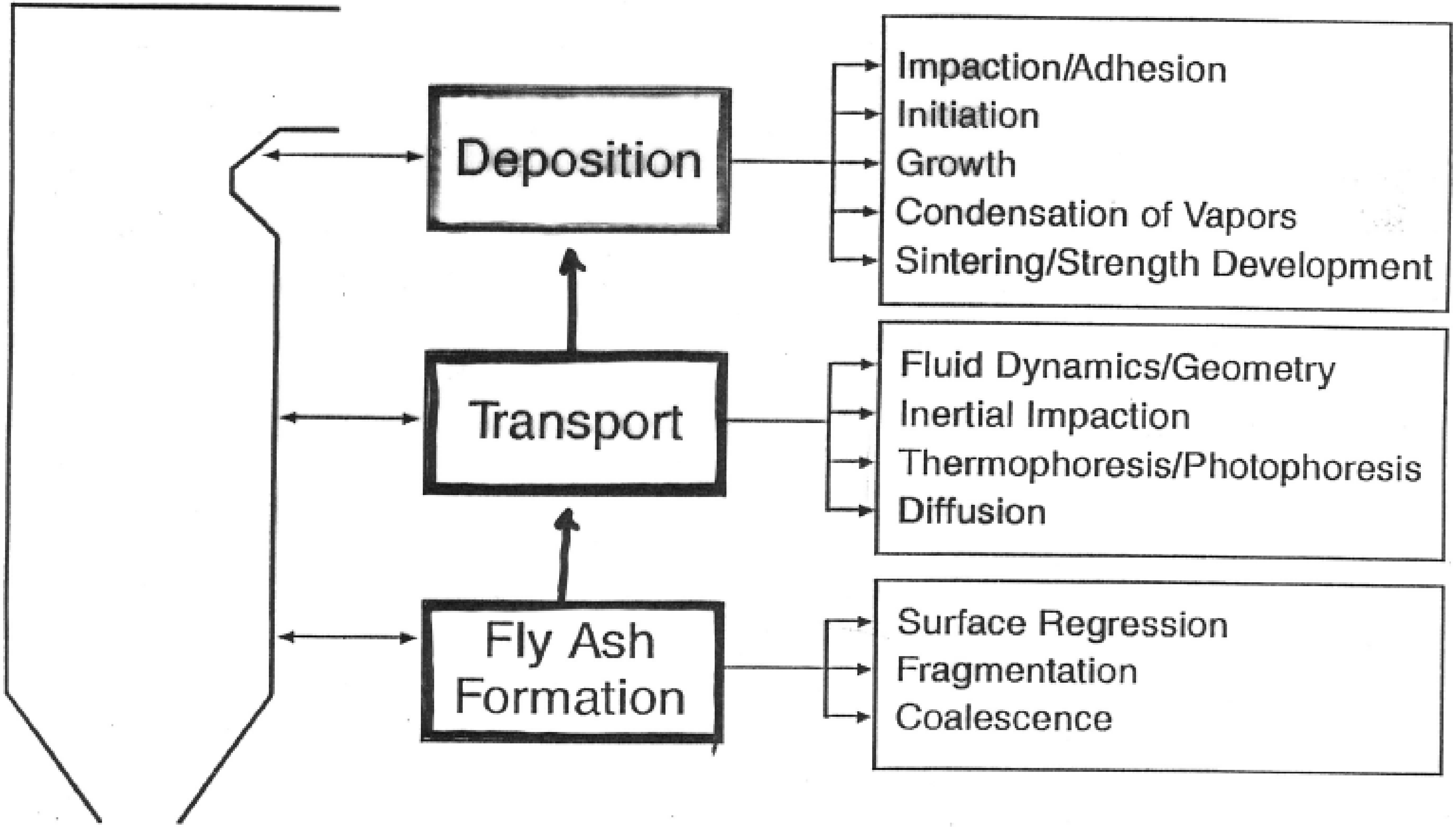
Convective Section

- Greater residence time
- Lower temperature
- More uniform y_{O2}
- Complete burnout
- Vaporized minerals can be dominant
- Sulfation plays more dominant role



Concept:
Change in T and composition
With thickness of deposit

Key Deposition Processes



Deposition

- Impaction/Adhesion
- Initiation
- Growth
- Condensation of Vapors
- Sintering/Strength Development

Transport

- Fluid Dynamics/Geometry
- Inertial Impaction
- Thermophoresis/Photophoresis
- Diffusion

Fly Ash Formation

- Surface Regression
- Fragmentation
- Coalescence

Particle Impaction/Adhesion

Key Dependencies:

- Ballistics of impacting particles
- Viscosity (stickiness)
  - Impacting particle
  - Deposit surface
- Rebounding particles

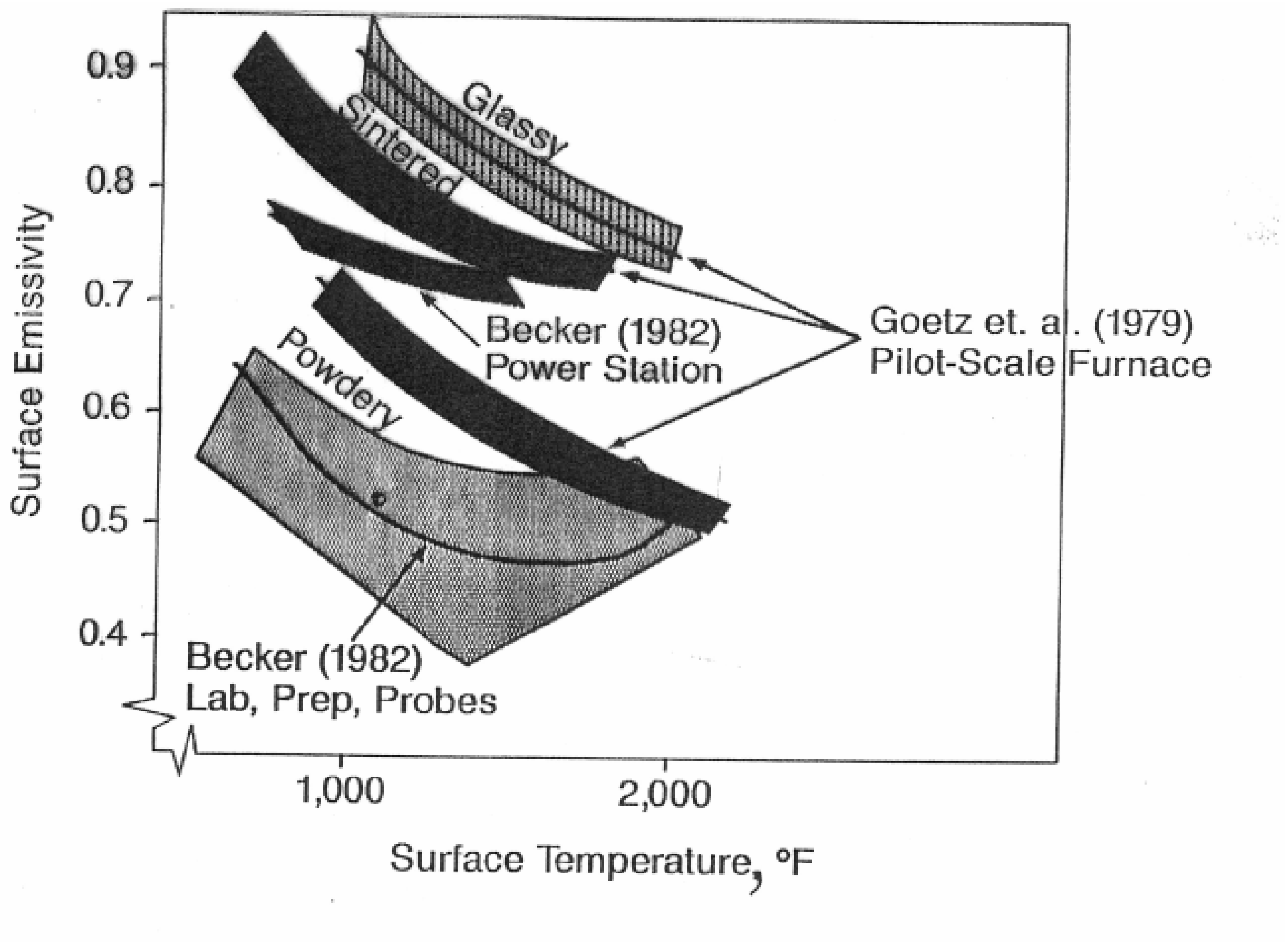
Challenges to Describing Impaction/Adhesion

- Particle viscosity calculation based on bulk ash composition
- Sticky surface due to vapor condensation
- Sticking of “dry” particles to sticky surface
- Surface temperature/stickiness of deposit
- Deposit sloughing

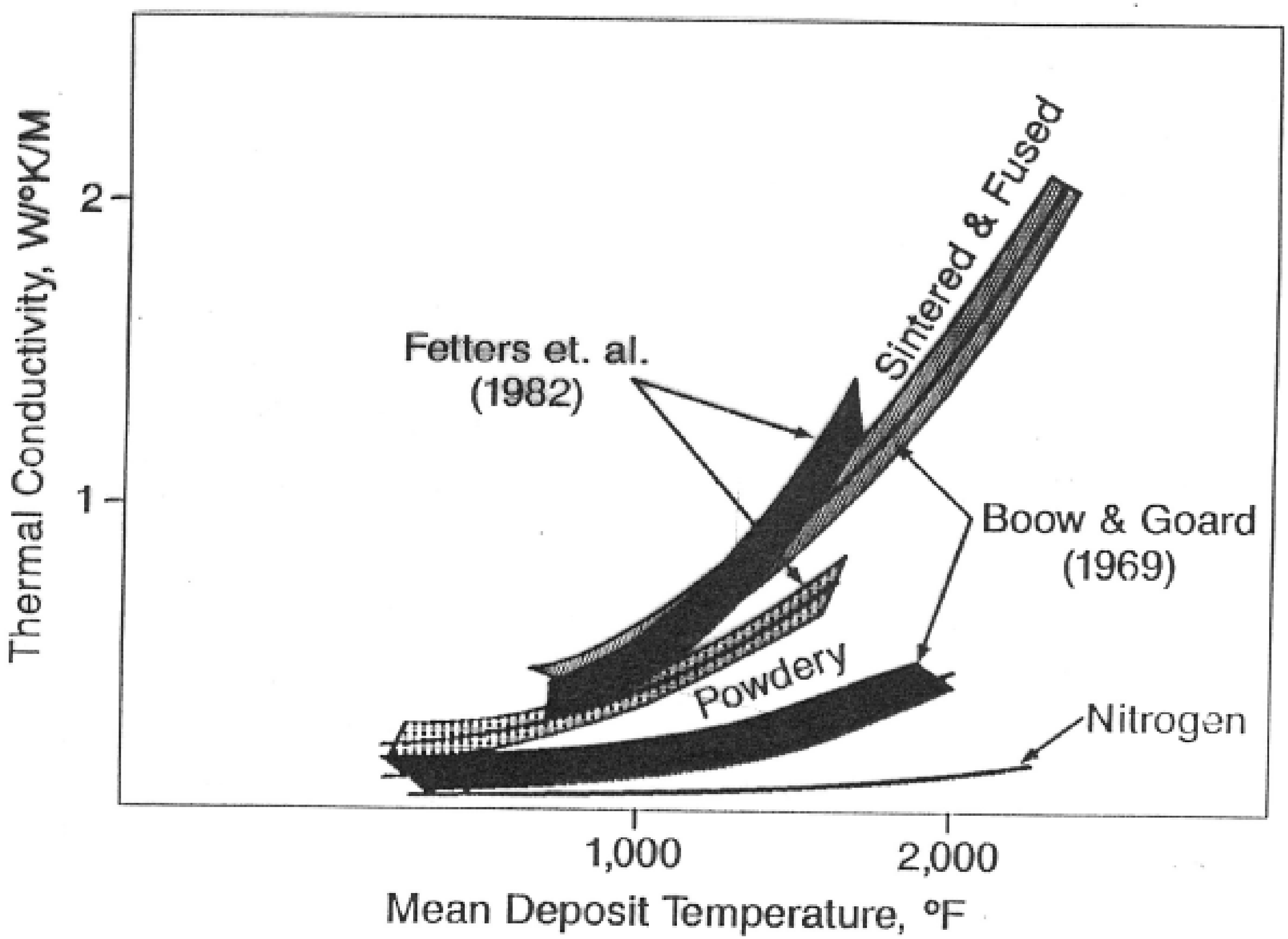
Deposit Characteristics

- Physical properties
  - Deposit-to-tube bonding
  - Deposit sinter strength
  - Physical state/viscosity
- Thermal properties
  - Radiant properties (emissivity, absorptivity)
  - Conductance (thermal conductivity, thickness)

Range of Deposit Emissivities



Range of Deposit Thermal Conductivities



Formation of Initial White Layer

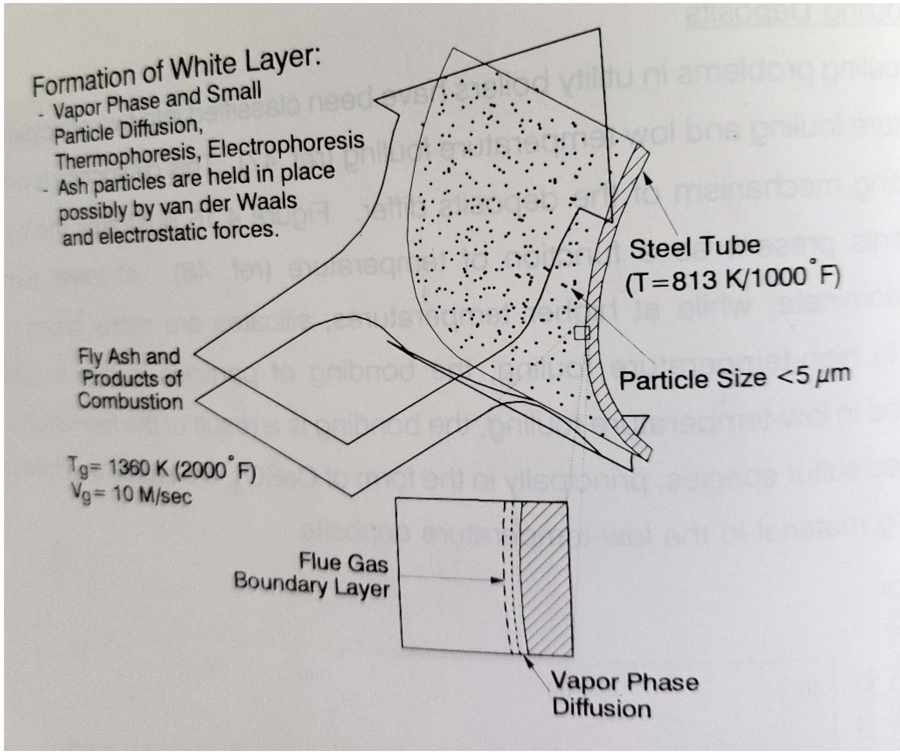


Fig. 4.17 Formation of initial deposit in fouling deposits

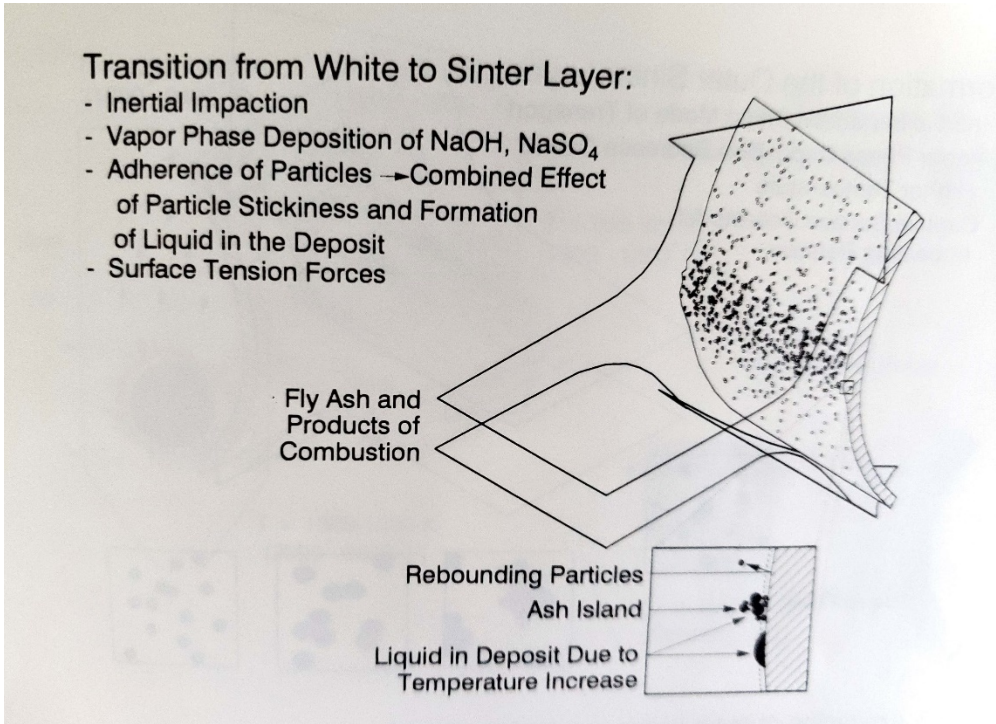


Fig. 4.18 Formation of transitional deposit layers in fouling deposits.

Formation of Outer Layers

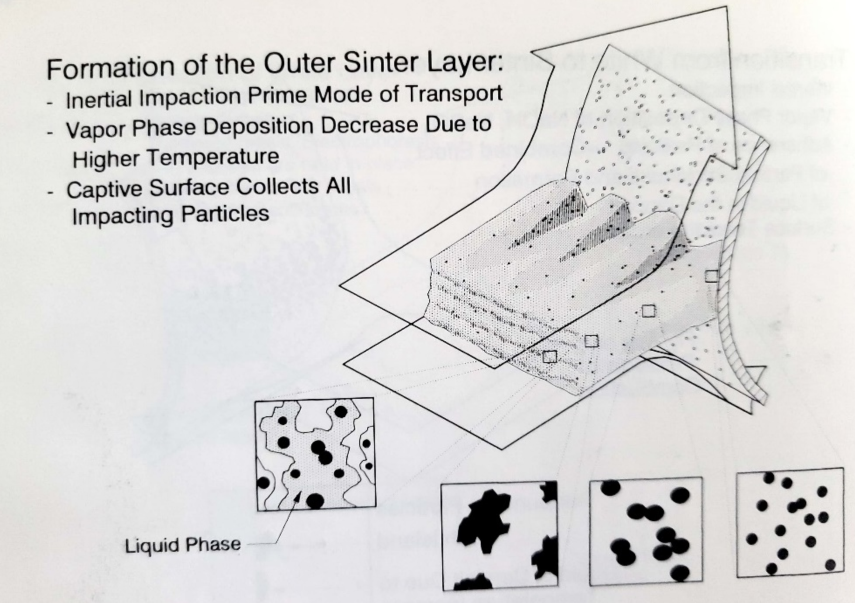


Fig. 4.20 Formation of outer layers in a fouling deposit.

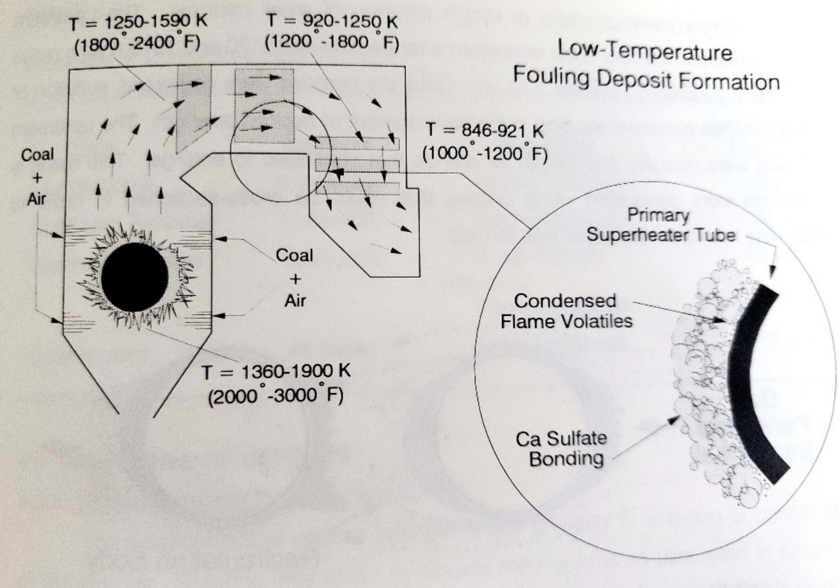
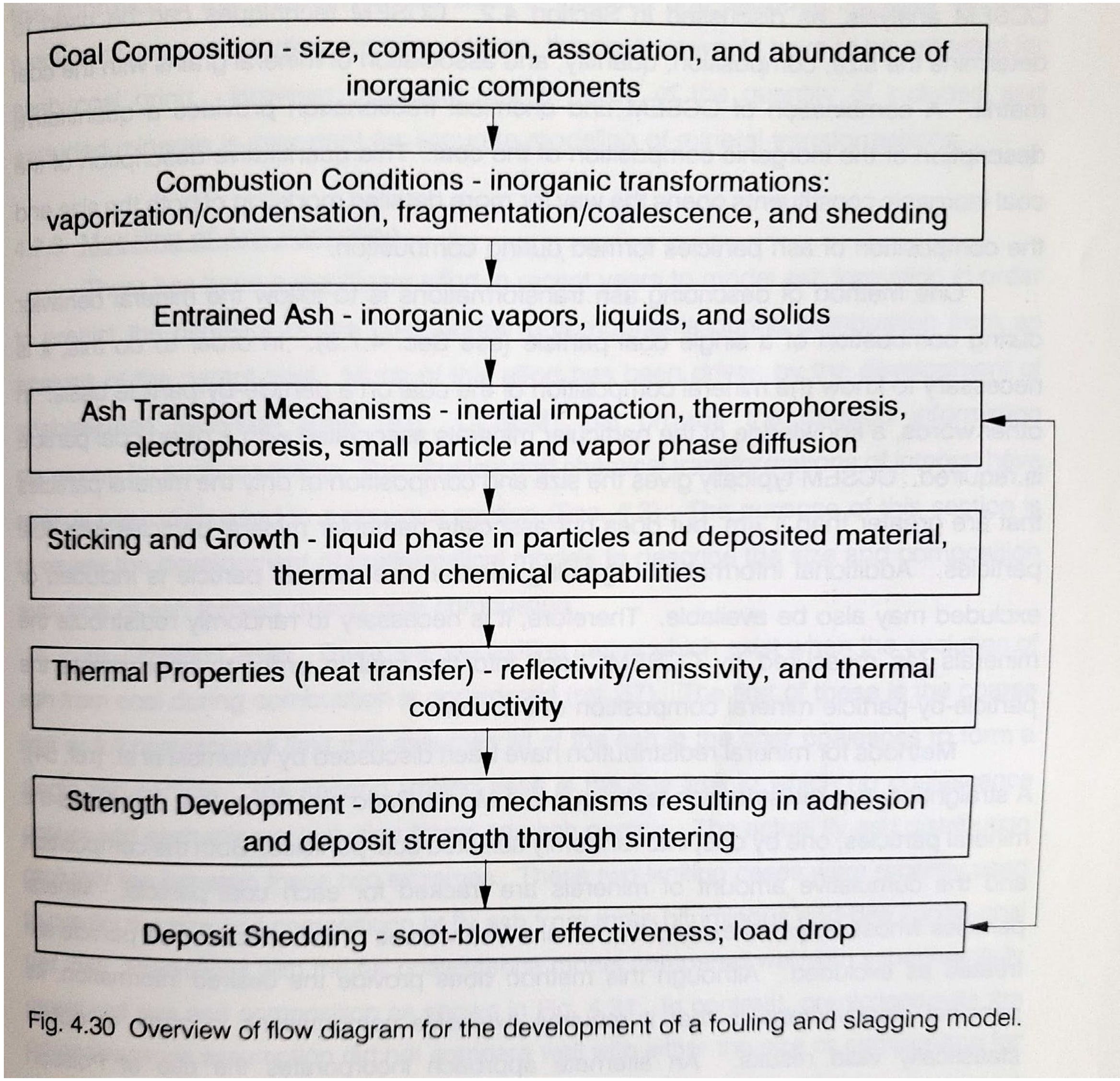


Fig. 4.22 Low-temperature fouling in utility boilers.

Overview of Fouling & Slagging Model



Coal Composition - size, composition, association, and abundance of inorganic components

Combustion Conditions - inorganic transformations: vaporization/condensation, fragmentation/coalescence, and shedding

Entrained Ash - inorganic vapors, liquids, and solids

Ash Transport Mechanisms - inertial impaction, thermophoresis, electrophoresis, small particle and vapor phase diffusion

Sticking and Growth - liquid phase in particles and deposited material, thermal and chemical capabilities

Thermal Properties (heat transfer) - reflectivity/emissivity, and thermal conductivity

Strength Development - bonding mechanisms resulting in adhesion and deposit strength through sintering

Deposit Shedding - soot-blower effectiveness; load drop

Fig. 4.30 Overview of flow diagram for the development of a fouling and slagging model.

Ash Disposal

1. Landfill ---> Getting harder to do
2. Cement ---> Needs low C in ash
3. Roadfill ---> Low level radiation?

High C in ash (> 10%)

- Gray ash
- Decreased ESP performance
- Loss of efficiency

Example: 10% ash in parent coal

$$Burnout\,(daf) = \frac{1 - \dfrac{x_{a,0}}{x_a}}{1 - x_{a,0}}$$

a. 20% C in ash ---> 97.2% daf burnout
b. 10% C in ash ---> 98.8% daf burnout
c. 5% C in ash ---> 99.4% daf burnout

Coal Cleaning (Why?)

A. Reduce Sulfur!!!!!

(Pyrite may occur in excluded mineral grains)

- Clean air act says SO_x must be decreased
- Eastern coals have a lot of sulfur
- Power generation needed in East
- Transportation of western coals is $$, even though they are low in sulfur

B. Reduce mineral matter

- less ash ---> less deposits)

Coal Cleaning (Methods)

A. Wash with H2O

B. Microbubble Flotation Process (MFP)

- finely ground coal (< 44 μm)
- mix with water in a column
- froth with air bubbles (d_b ~ 100 μm)

C. Spherical Oil-Agglomeration Process (SOAP)

- finely ground coal (< 44 μm)
- mix with water
- mix with heptane
  (binds coal together into 1 mm particles)
- steam treat to remove heptane
  (50 ppm to 0.2 wt% heptane in final SOAP product)

D. Molten Caustic Leach

- molten NaOH bath ($$, reduced volatiles)

Coal Cleaning
(Effects on Combustion)

A. Less sulfur (but not a whole lot -- mainly excluded pyrite grains)

B. Less ash

   - Some ash needed for boiler operation (bare tubes have different emissivity)

C. Possible enrichment of Fe and other species in ash may cause difficulty in removal of deposits

Question 8

- Suppose we knew everything about mineral matter deposition, including all of the chemistry, particle sizes, velocity patterns, and temperature distributions. What could we do with this information to make money?

Ideas

- Determine bad coals for a certain boiler
- Frequency of sootblowing
- Areas of boiler prone to corrosion
  - Better steel in those areas?
  - Frequency of shutdown
- Heat transfer calculations improved
- Impact of additional fuels
  - Biomass, etc.

So What Should I Remember About Mineral Matter?

- Importance
  - Combustor size
  - Heat transfer
- General occurrence of minerals in coals
  - Included vs excluded
  - major elements and species
- Techniques for analysis
  - CCSEM
  - chemical fractionation
  - ICP
  - There are others (XRF,XANES, etc.) that were not discussed
- Reaction pathways
- Slagging vs. Fouling
- Crystaline matrix (glass) modifiers (Na, K, Ca, Fe)
- Ternary diagrams
- Fly ash distributions & fragmentation
- Sootblowing
- Coal cleaning (approaches & problems)

Coal Cleaning

(Test Results in Pilot Scale Combustor)

- Ash reduced by ~ 50%
- Si in ash decrease, Al same, all other elements increased
- Inorganic size distribution unaltered
- Waterwall heat transfer increased (thinner deposits due to lower ash content)
- Waterwall cleanability remains same
- Less erosion in convective pass (less Si ---> less quartz)
- Less steam tube fouling (less ash)
- Fouling deposits harder to clean (increased Fe)
- Char oxidation about the same (depending on which investigator you believe) ---> no problem