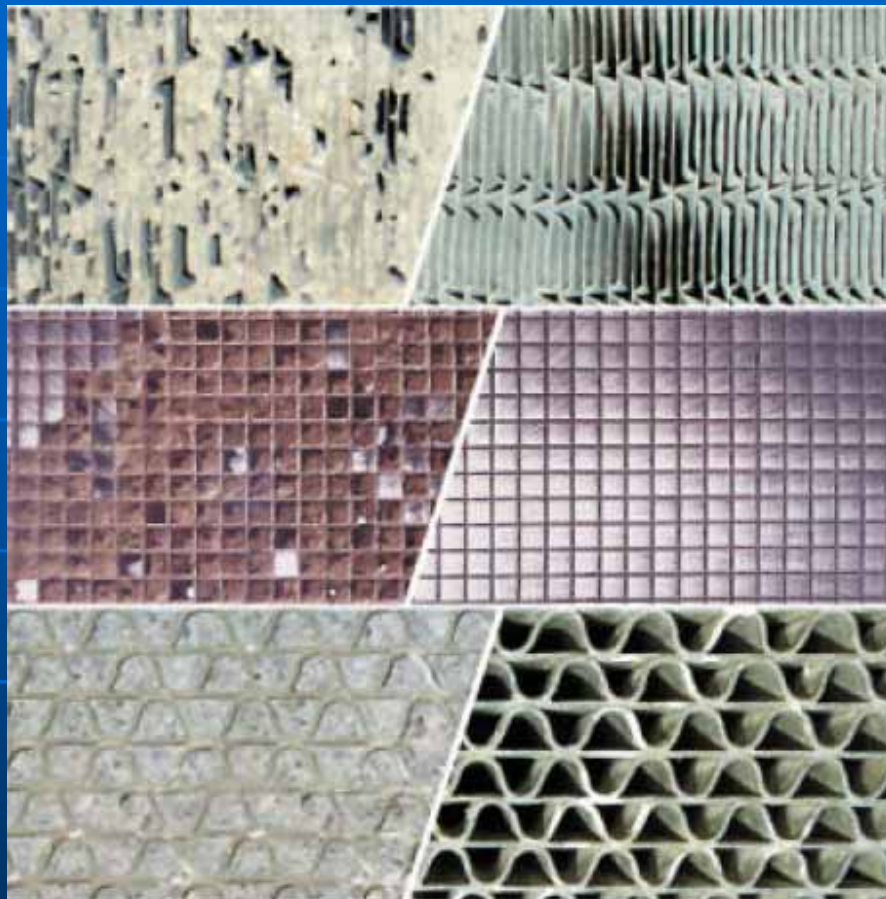


SCR CATALYST POISONING

*2006
NOx/PCUG
Conference,
January 23-26*

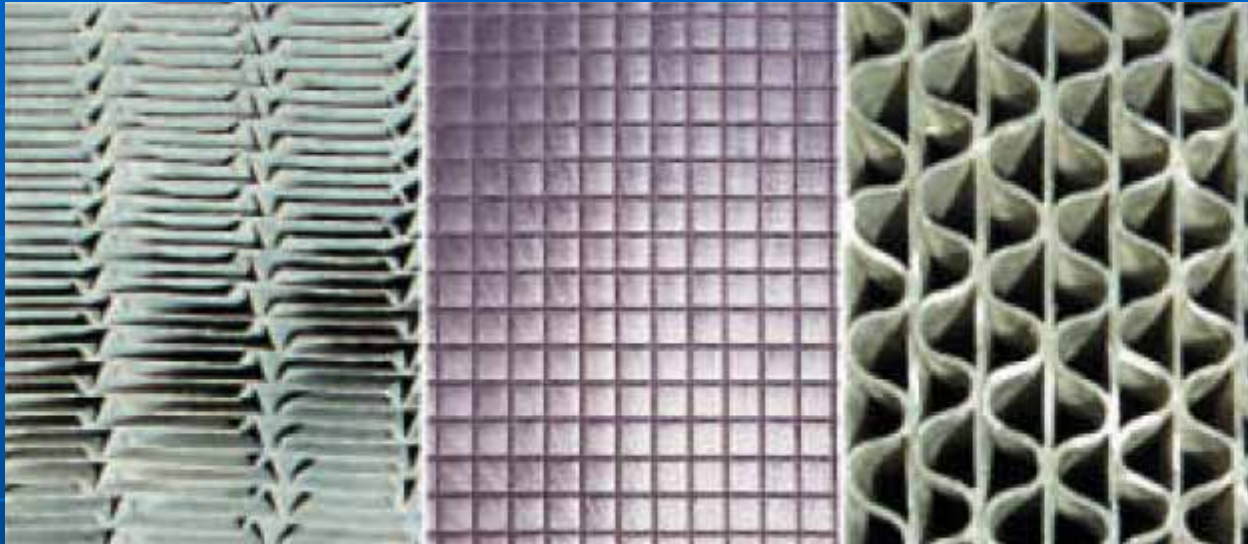


*Presented by: W. Scott Hinton, Ph.D., P.E.
Technical Director – Mercury Research Center
Southern Research Institute
850-936-0037 hinton@sri.org*

OUTLINE

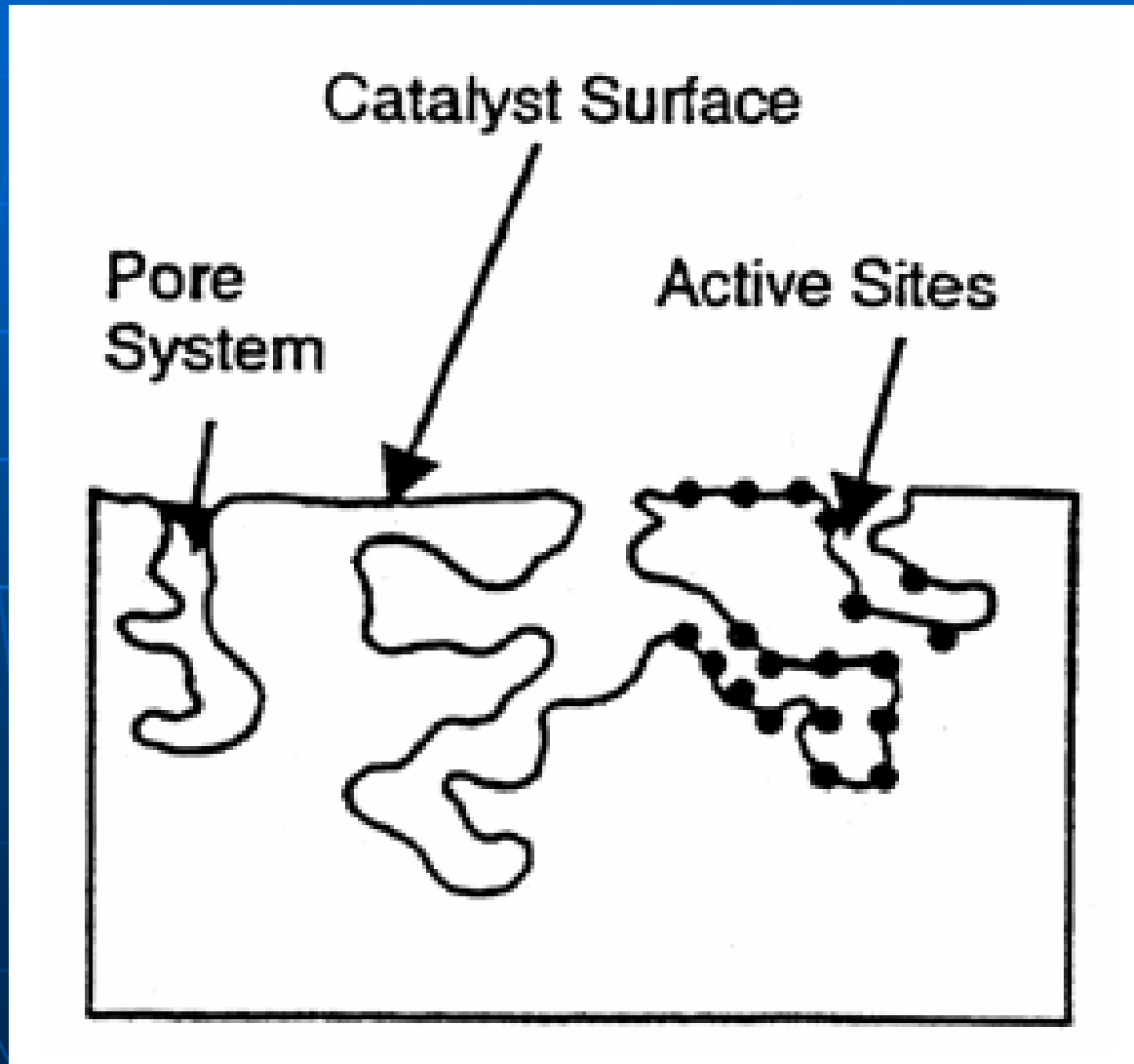
- **CATALYST BASICS**
- **POISONING MECHANISMS**
- **EASTERN BITUMINOUS COALS**
- **POWDER RIVER BASIN COALS**
- **SPECIAL POISONS AND FUELS**
- **UPDATE: MERCURY AND SCR CATALYSTS**

CATALYST BASICS

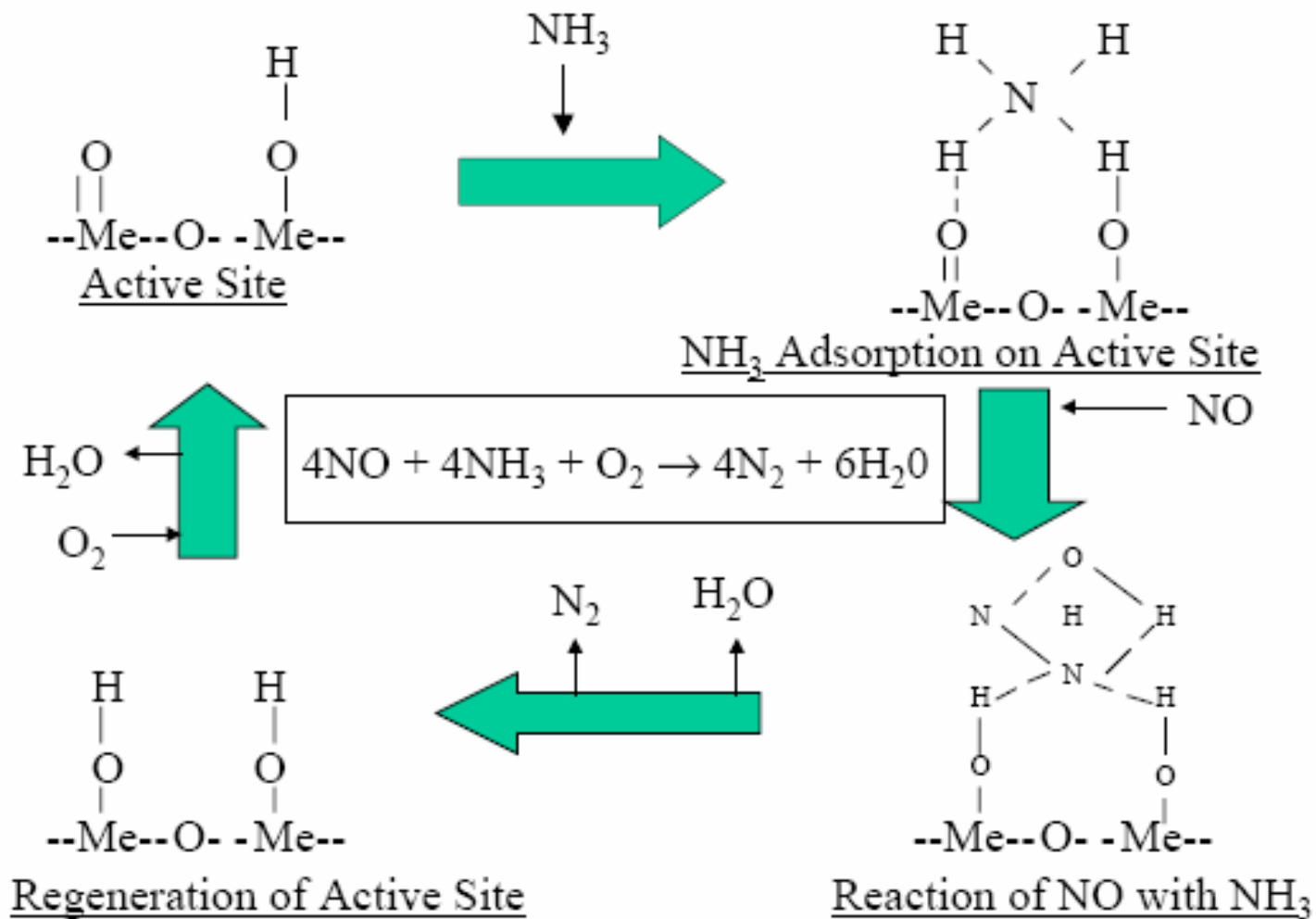


- Three General Geometries; Plate, Honeycomb, Composite/Hybrid
- Composition; Titania catalyst support with Vanadium as principal active component, other promoters, etc. added (Tungsten, etc.)
- Physical strengthening with screens, fibers, etc. in some designs

MICROSCOPIC CATALYST PROPERTIES



MECHANISM OF NO_x REDUCTION



POISONING/DEACTIVATION MECHANISMS

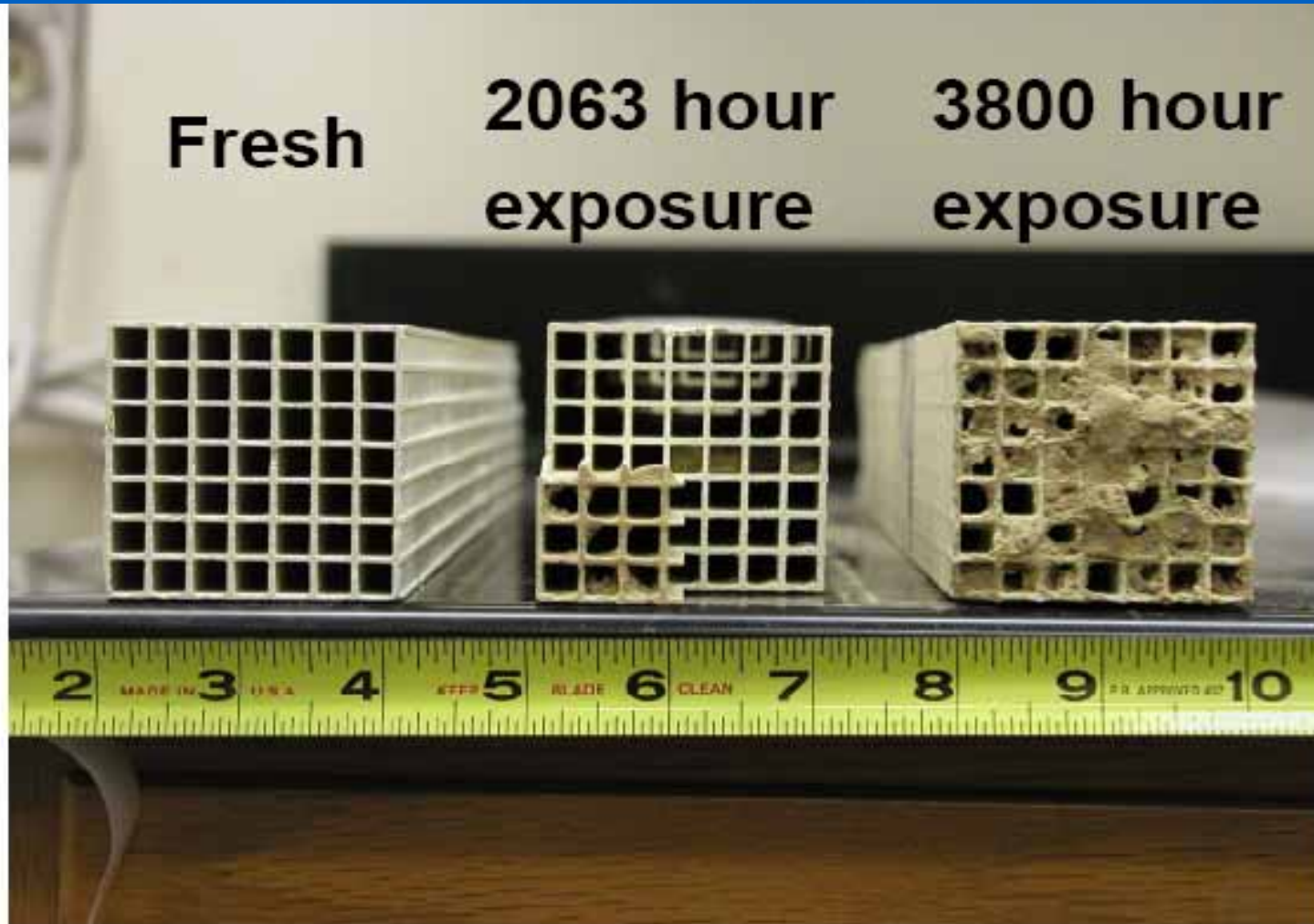
➤ PHYSICAL

Characterized by physical blockage of pores or channels preventing reactants from accessing the catalyst active sites. Examples; general fouling, calcium sulfate masking

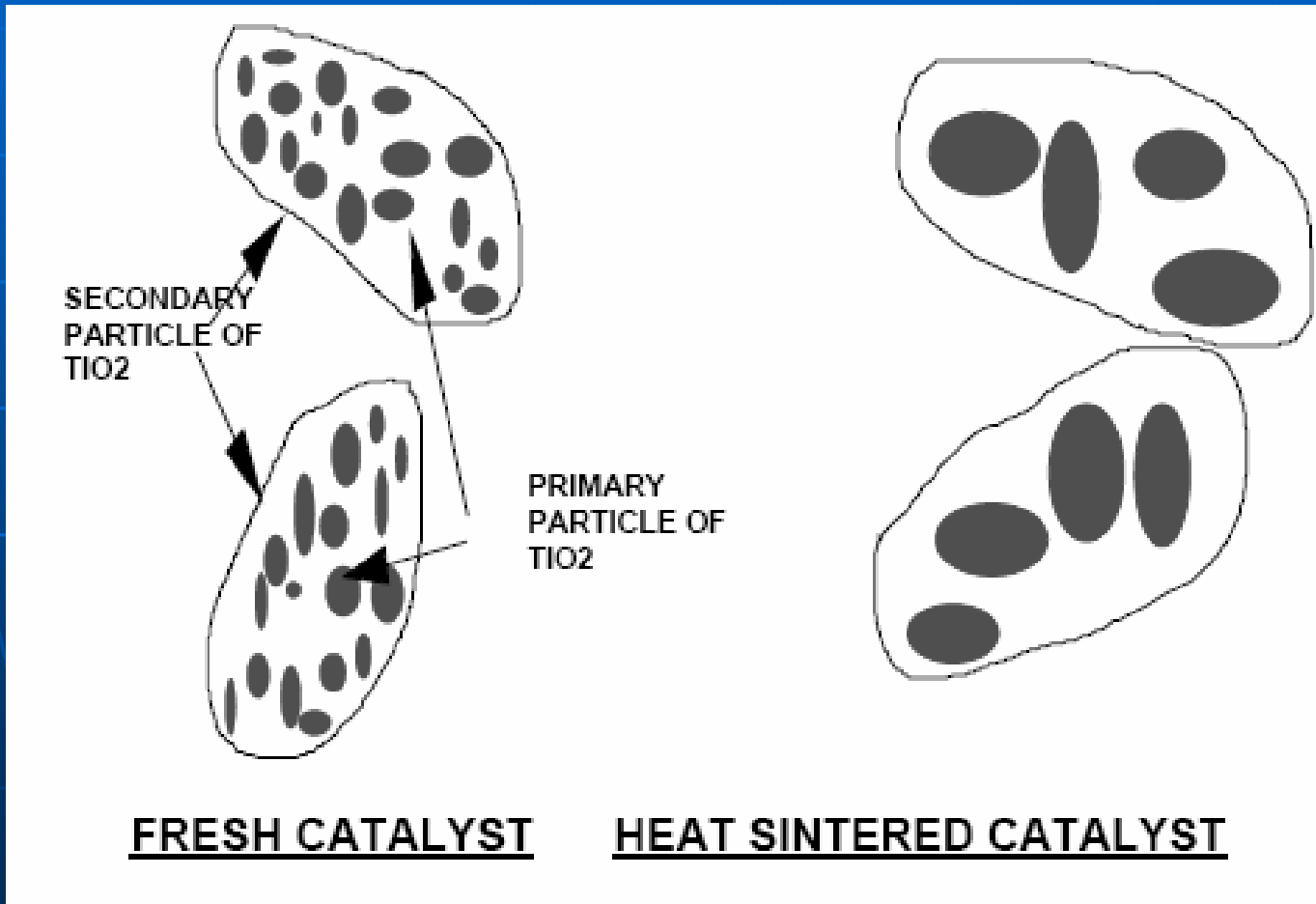
➤ CHEMICAL

Characterized by chemical attack on active vanadium sites. Examples; arsenic poisoning, sodium, potassium, and phosphorus poisoning

GENERAL FOULING

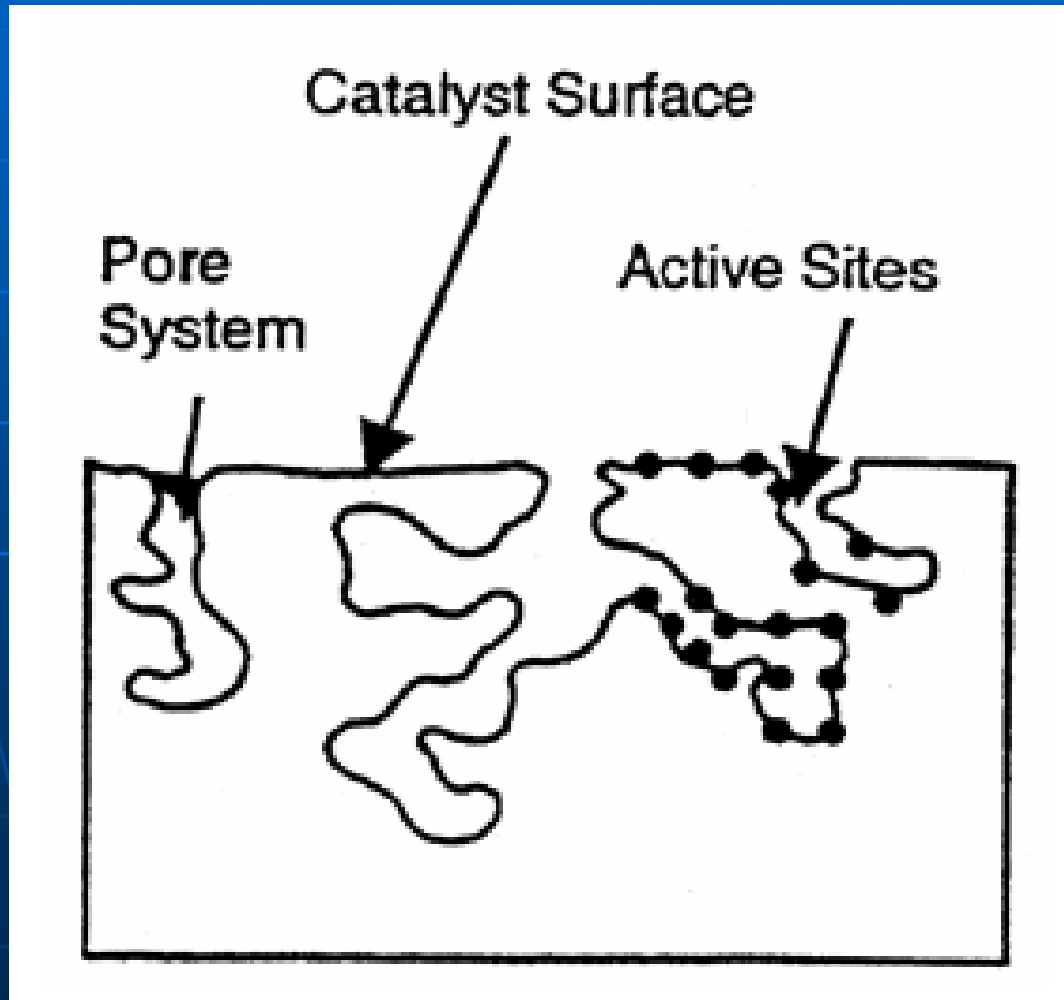


HEAT SINTERING



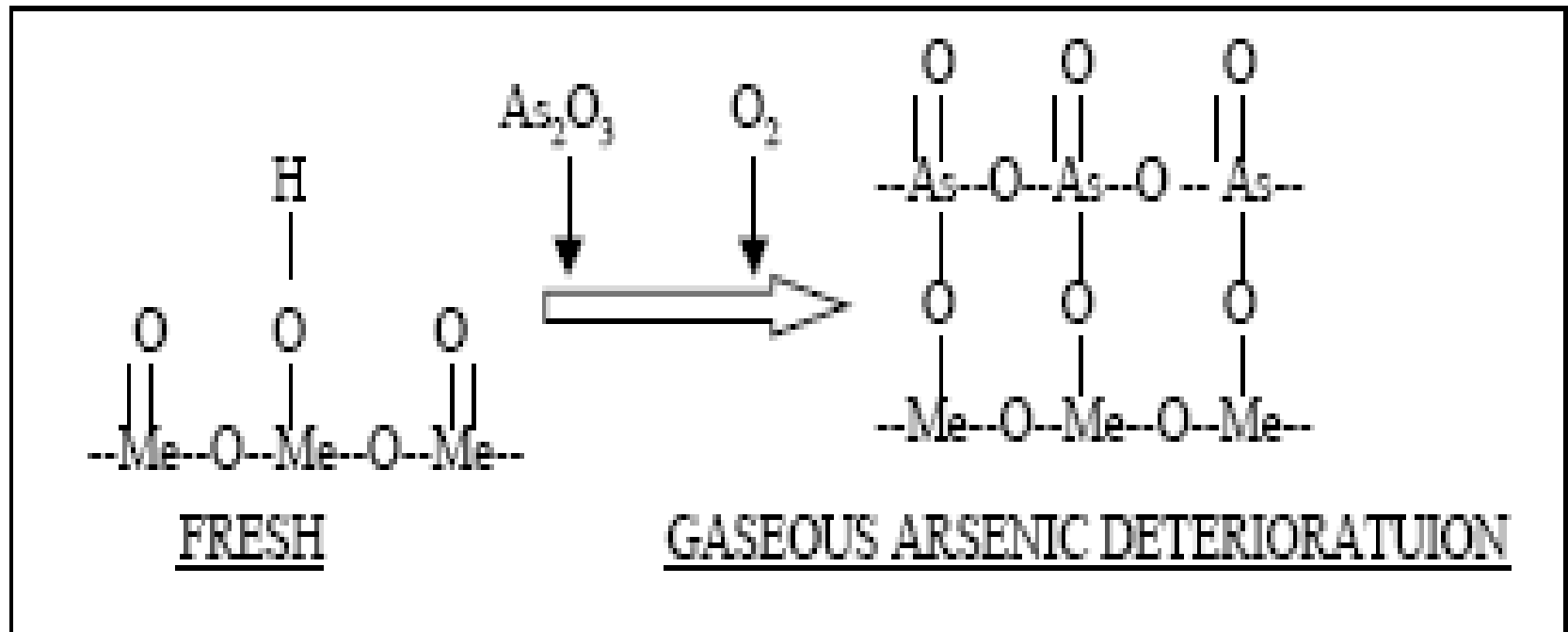
CHEMICAL POISONING

-Gaseous compounds attack active sites-

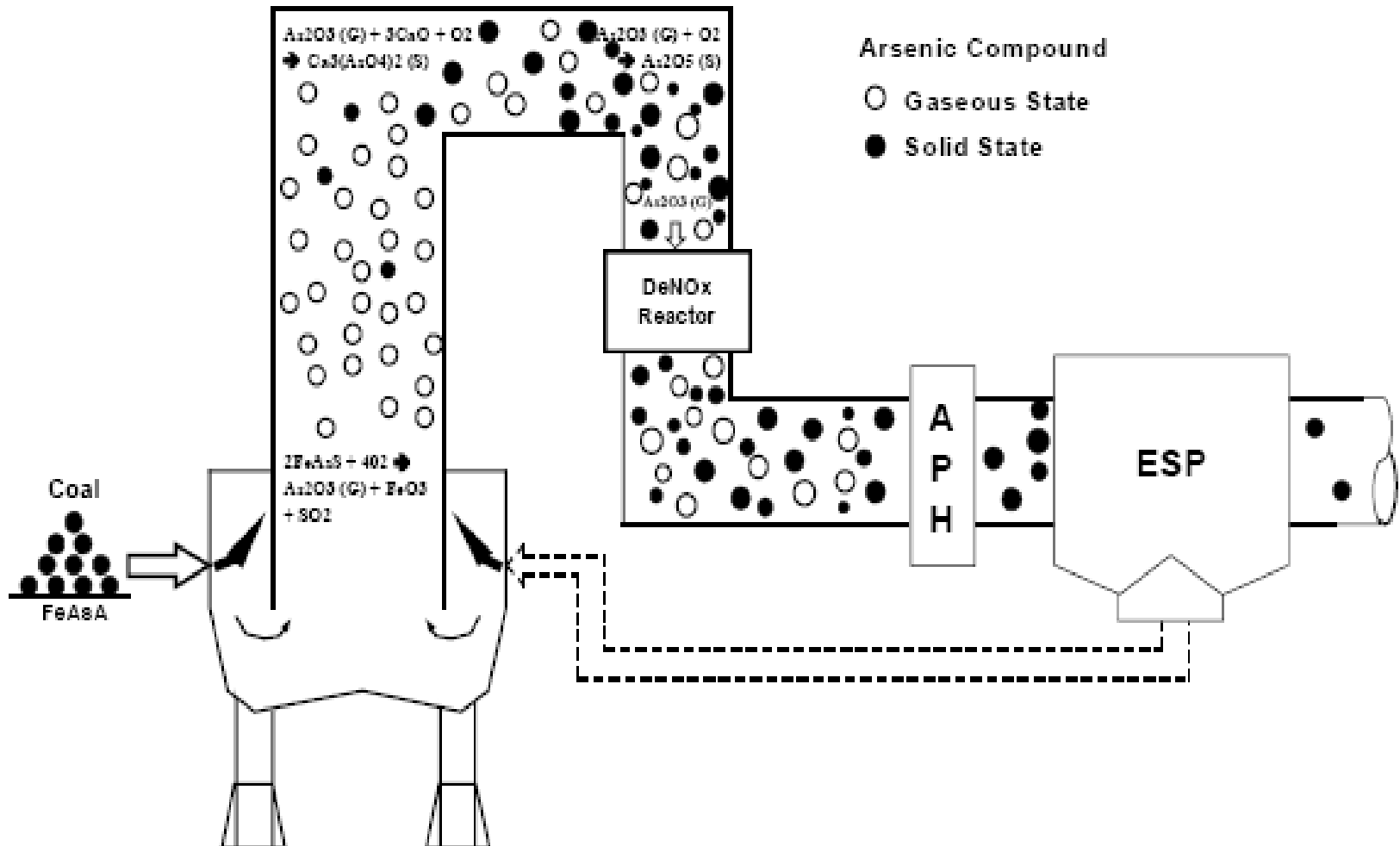


See Reference. #1

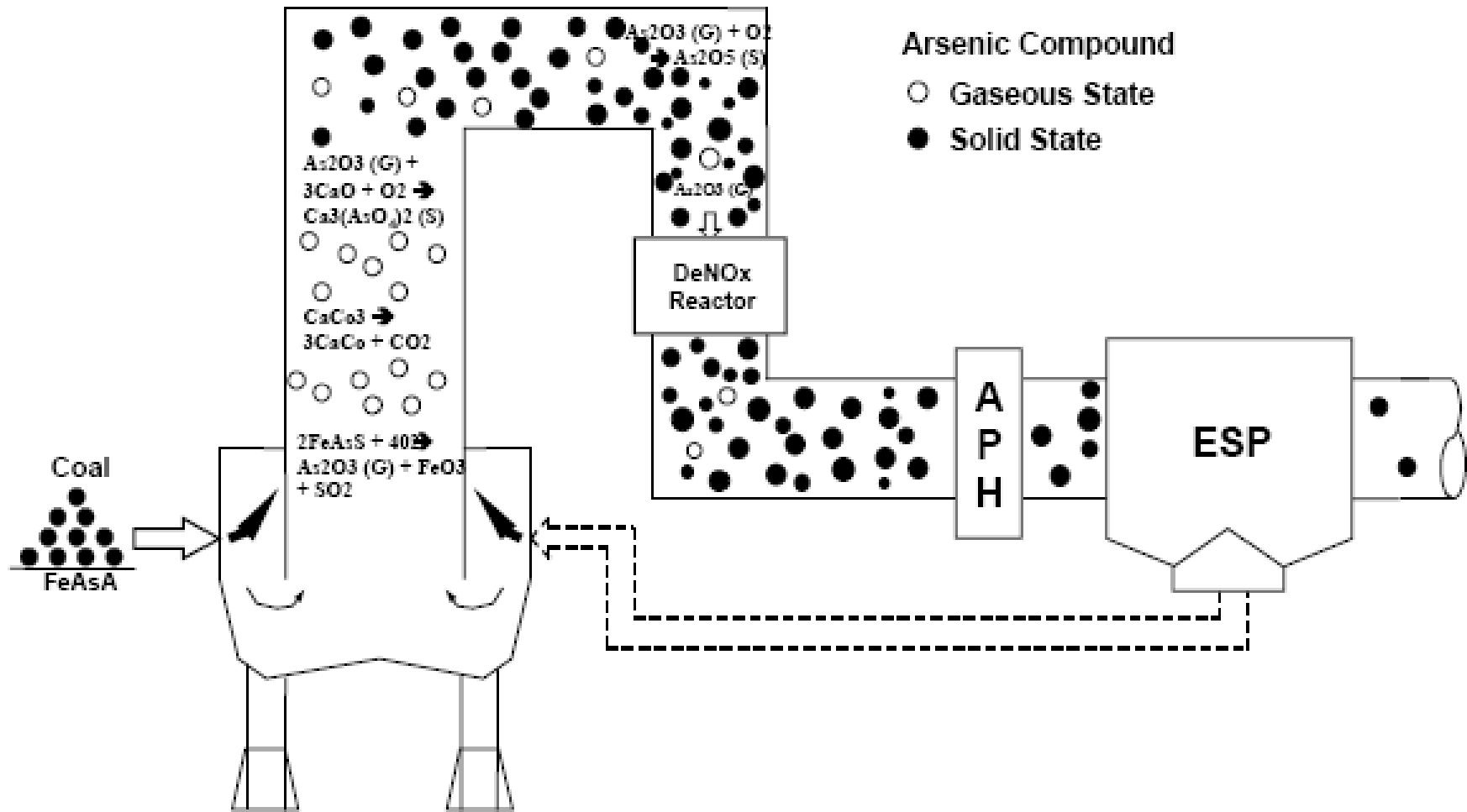
EASTERN BITUMINOUS COAL CHEMICAL POISONING - ARSENIC



GASEOUS ARSENIC IN FLUE GAS TRAIN

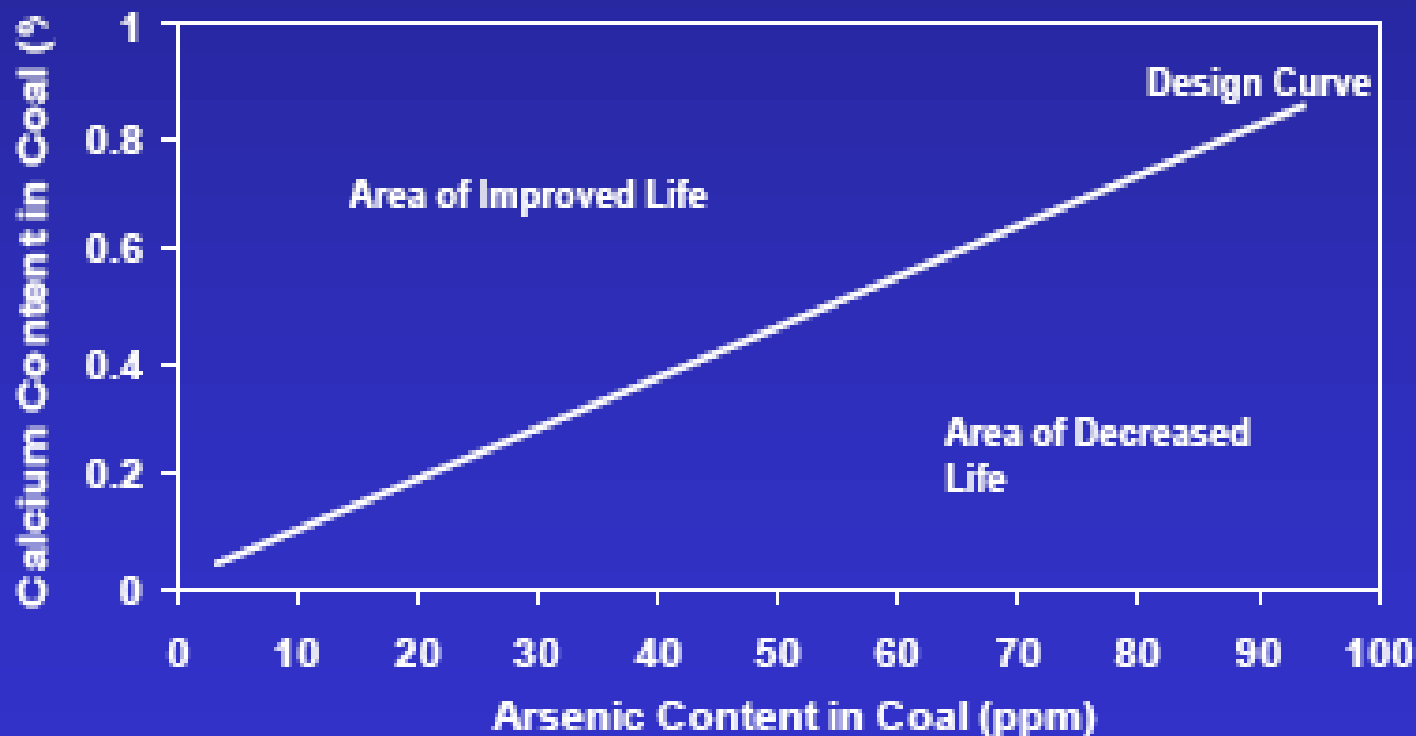


EFFECT OF CALCIUM ON GASEOUS ARSENIC



Effect of Calcium on Arsenic Poisoning and Catalyst Life

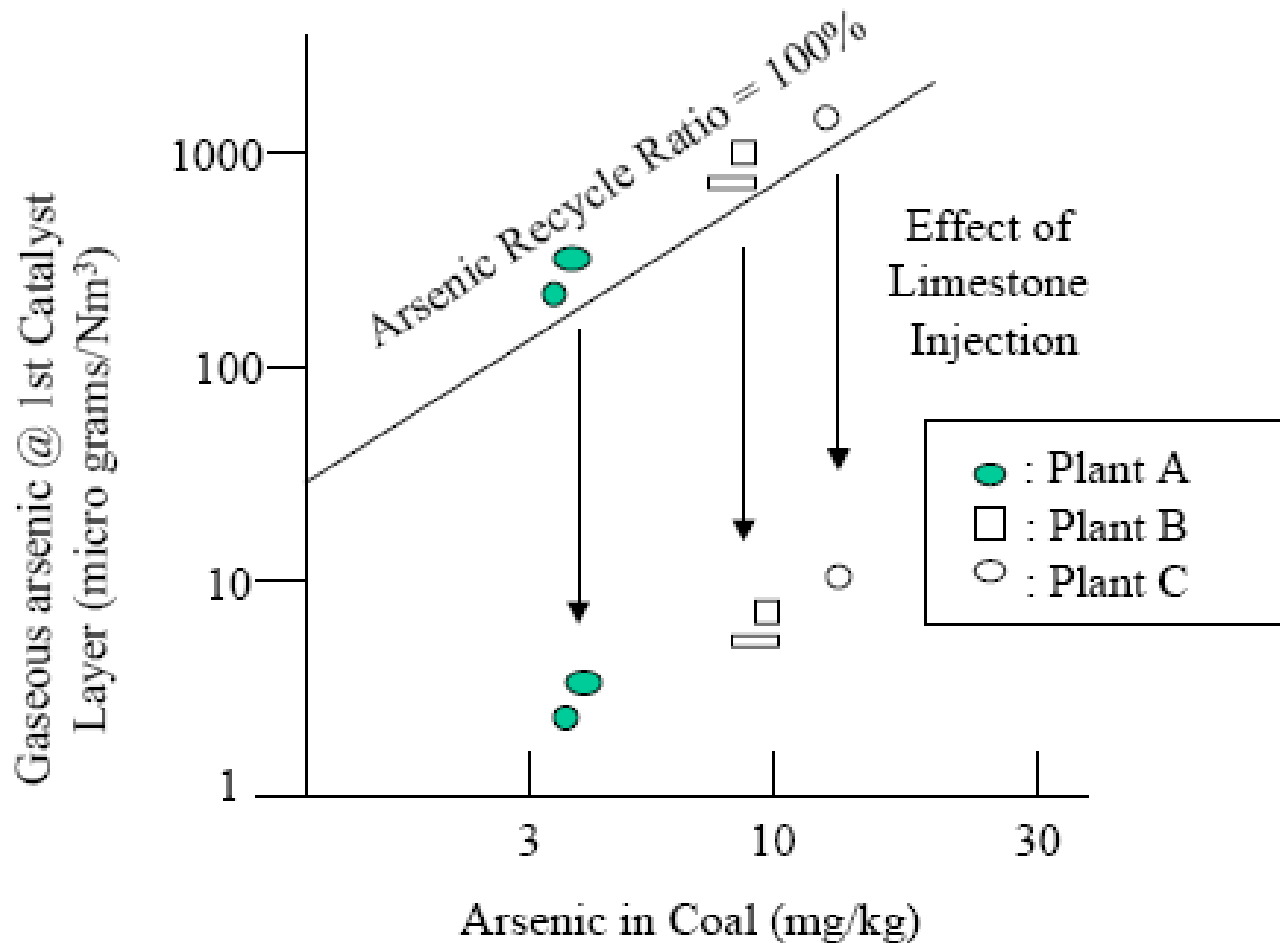
Catalyst Life vs. Arsenic and Calcium in Fuel



MITIGATION STEPS FOR ARSENIC POISONING

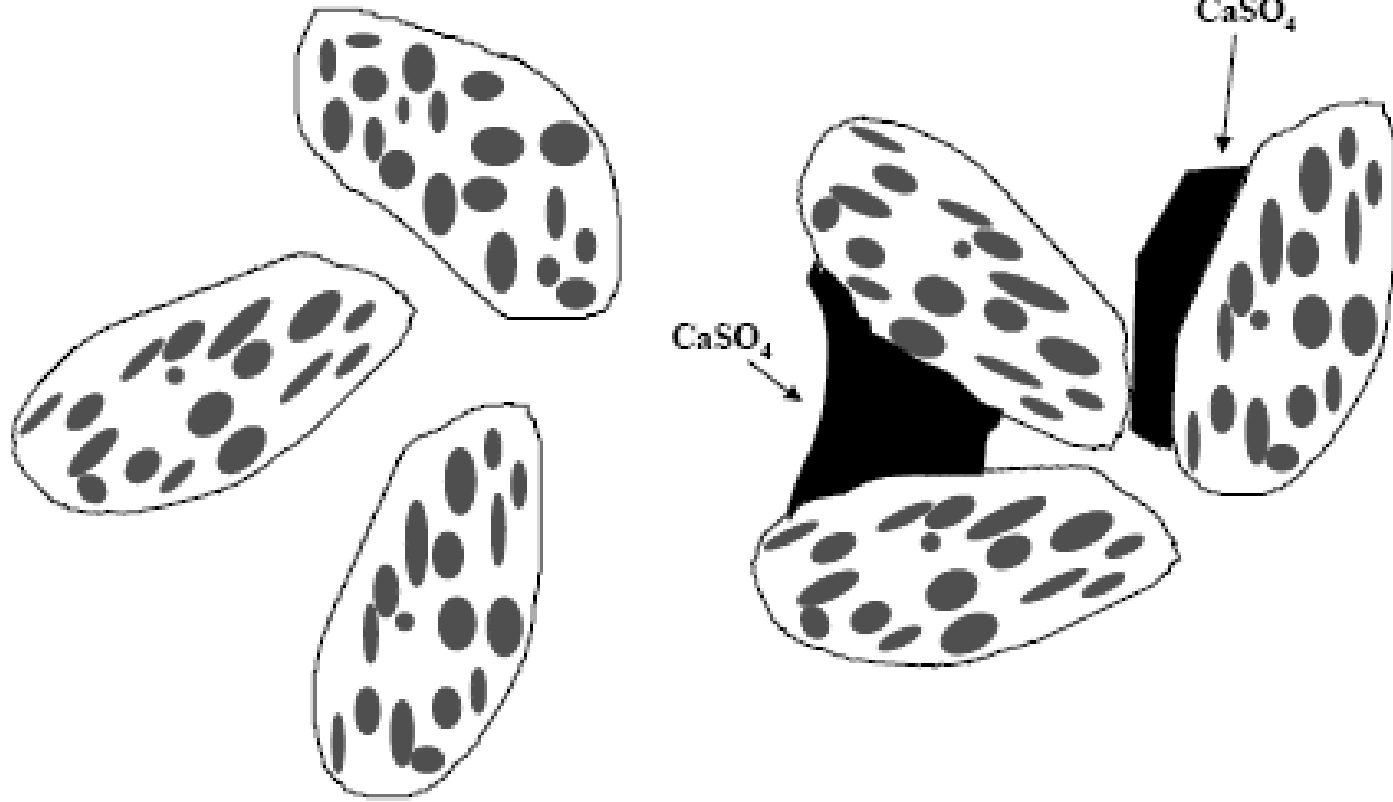
- MORE CATALYST VOLUME and/or ACTIVITY (MARGIN)
- POISONING RESISTANT CATALYST DESIGN
- FUEL SELECTION
- CALCIUM/LIMESTONE ADDITION

EFFECT OF LIMESTONE ADDITION



POWDER RIVER BASIN COAL

PSEUDOCHEMICAL POISONING - CALCIUM

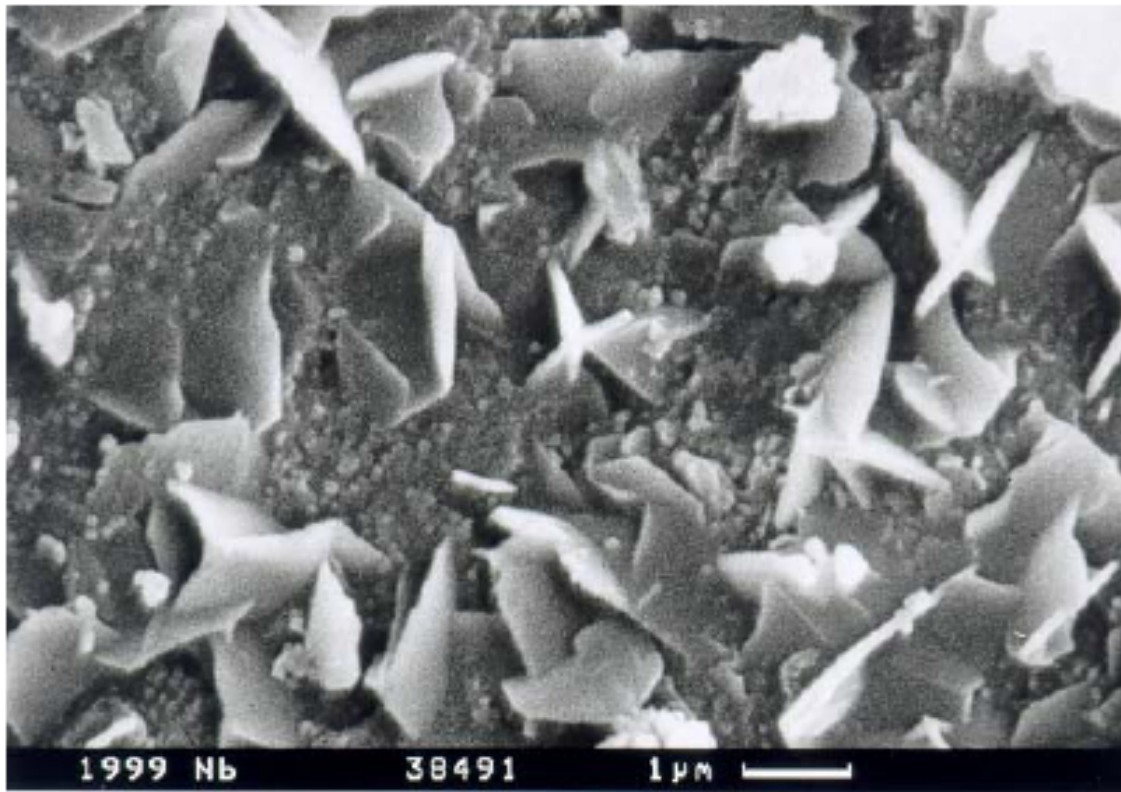


FRESH

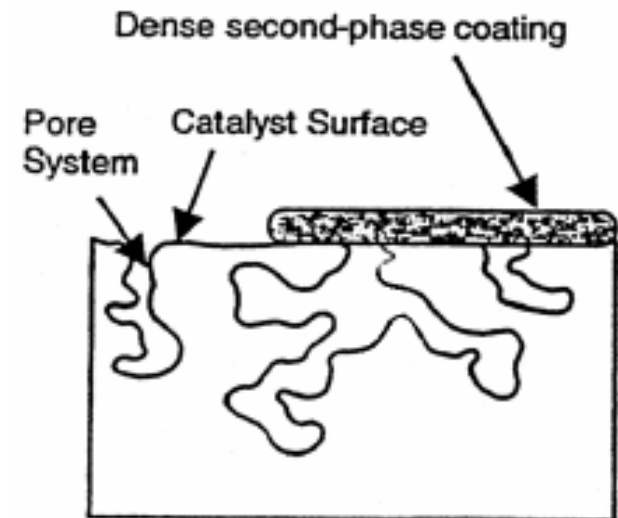
CALCIUM DETERIORATION

"PRB POISONING" MECHANISM

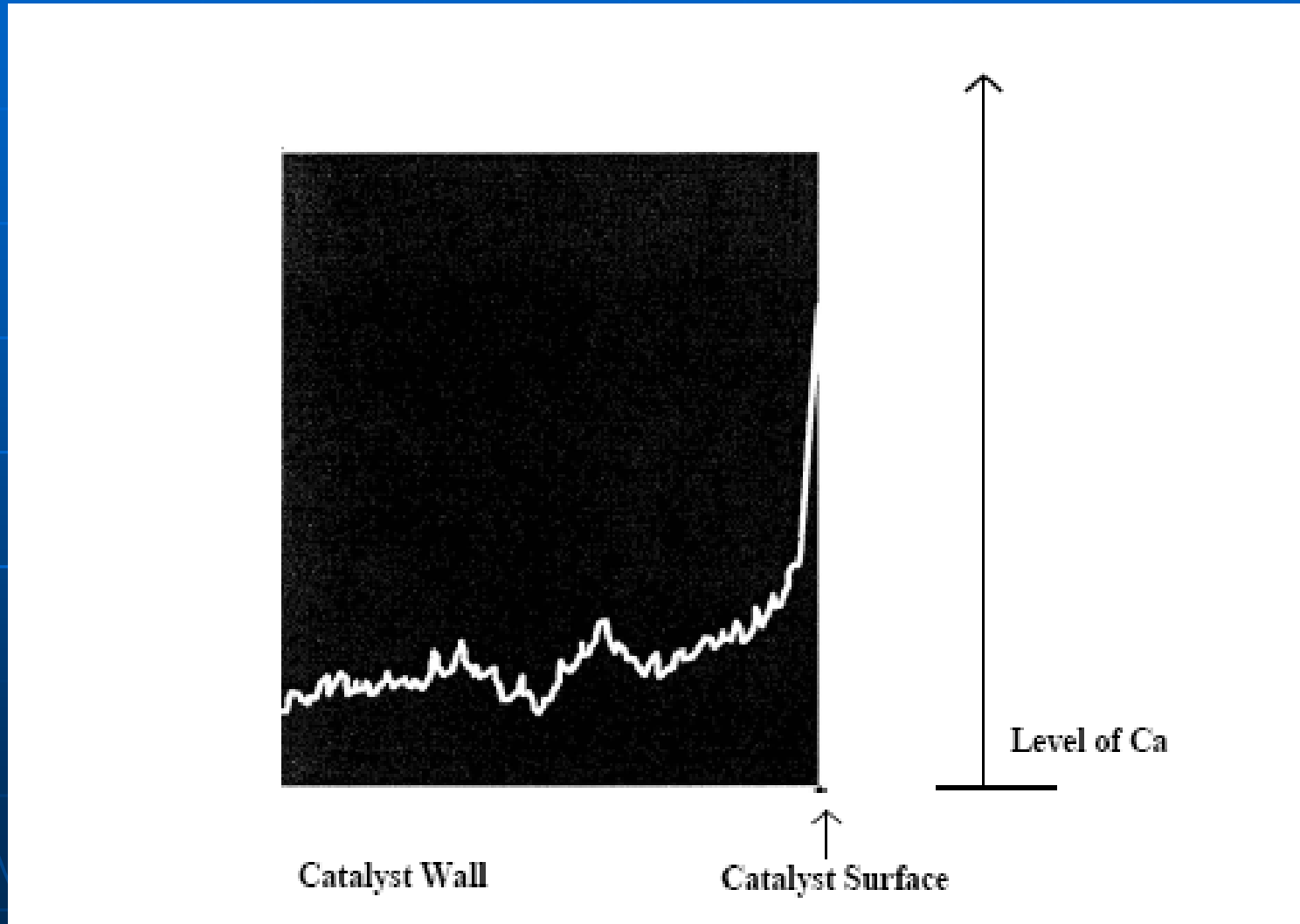
Calcium sulfate coating on catalyst surface



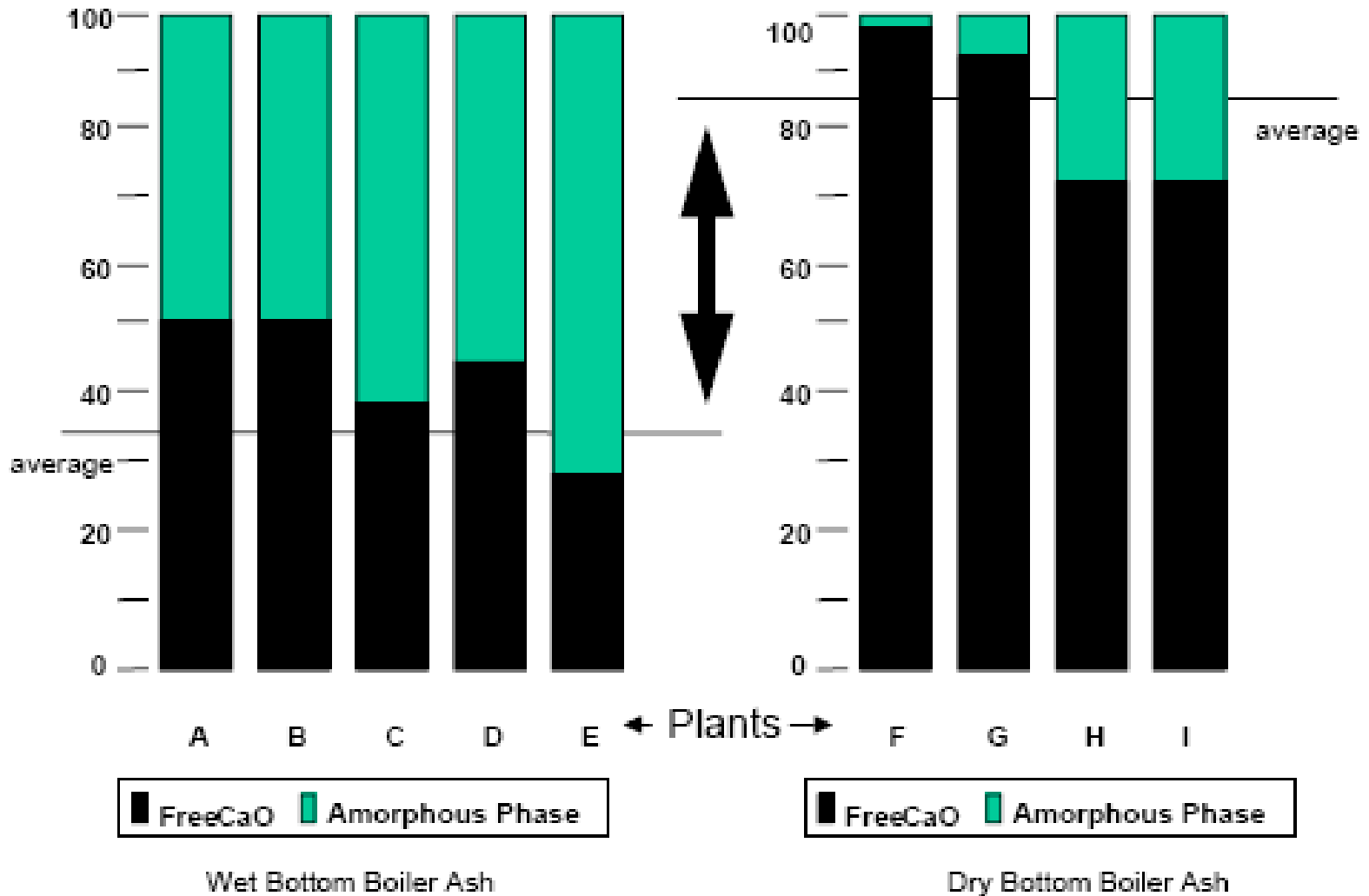
Masking:
Macroscopic blockage of catalyst surface by dense second-phase coating



ENRICHMENT OF CALCIUM AT CATALYST SURFACE



DRY BOTTOM vs. WET BOTTOM BOILERS (PRB COALS)



MITIGATION STEPS FOR PRB/CALCIUM SULFATE POISONING

- **MORE CATALYST VOLUME and/or ACTIVITY
(MARGIN)**
- **POISONING RESISTANT CATALYST DESIGN**

OTHER CHEMICAL POISONING SPECIES

➤ SODIUM (Na)

➤ POTASSIUM (K)

➤ PHOSPHORUS (P)

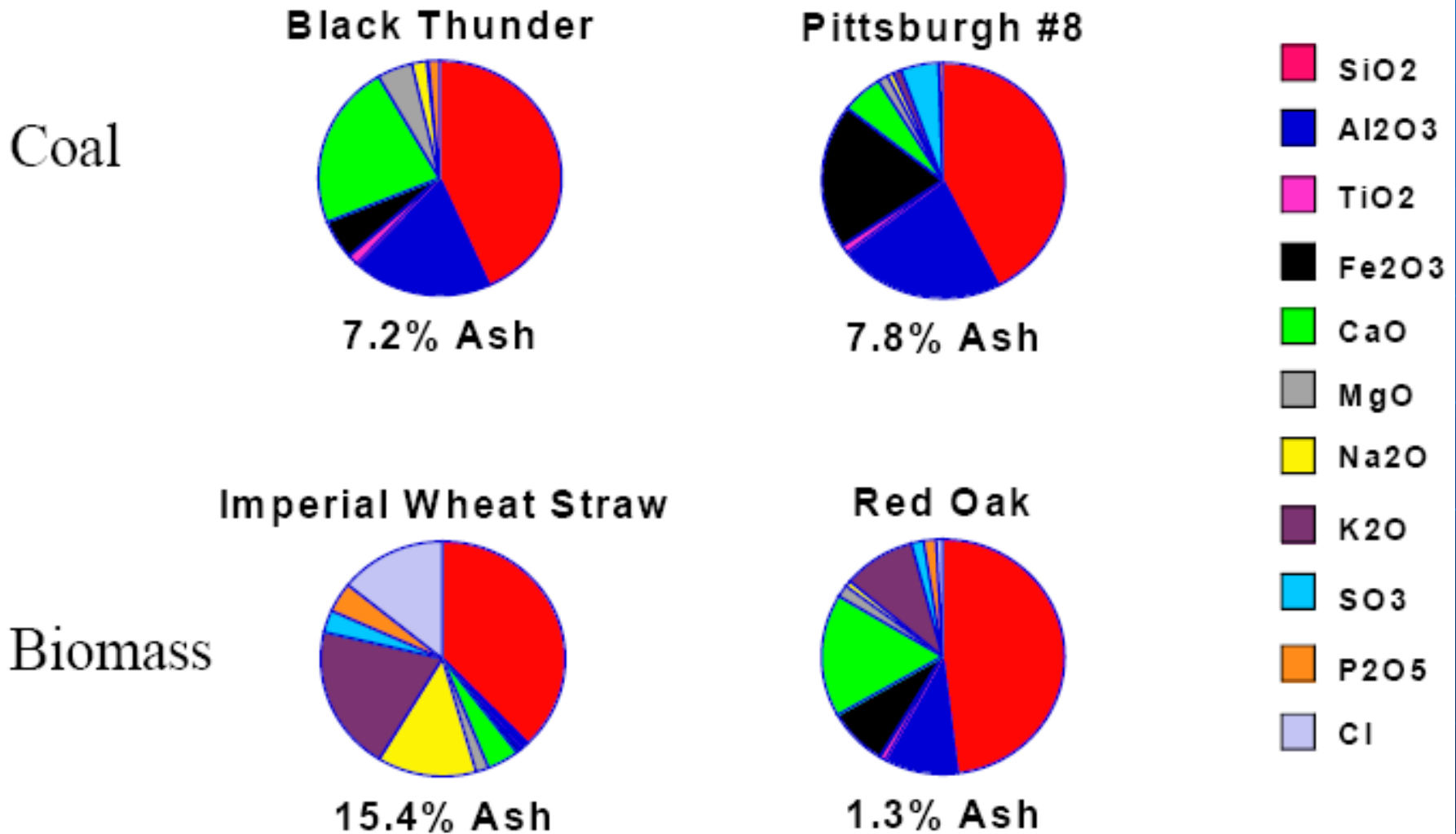
SOURCES OF SODIUM, POTASSIUM, AND PHOSPHORUS POISONING

➤ **PRIMARY FUEL**

➤ **BIOMASS CO-FIRING**

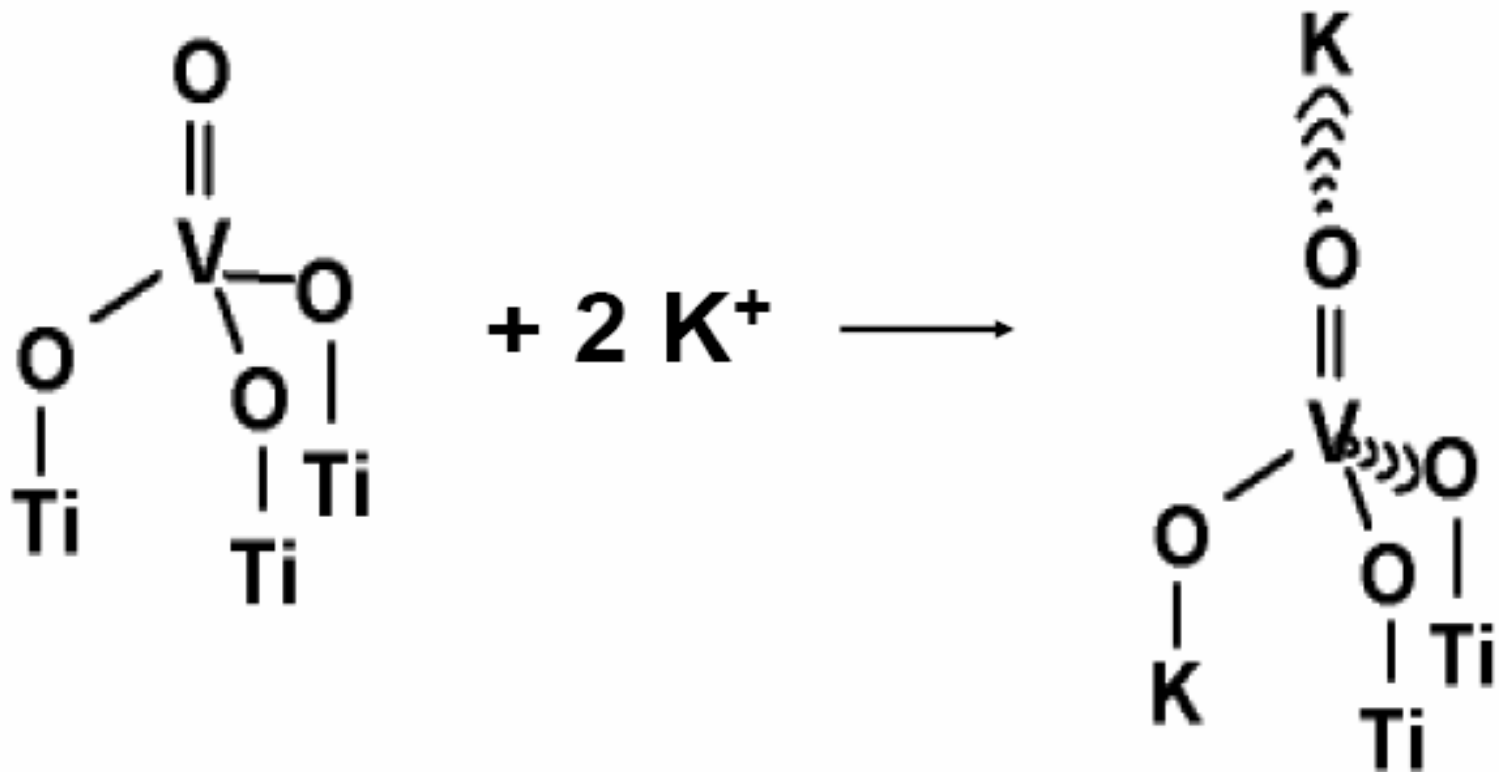
➤ **PROCESS SOURCES** (boiler water, wash water, fuel additives, paints, lubricants, etc.)

COMPARISON OF ASH CONSTITUENTS FOR DIFFERENT FUELS



MECHANISM OF CHEMICAL POISONING BY SODIUM AND POTASSIUM

Alkalis: Reactions with the acid V_2O_5 sites



SODIUM AND POTASSIUM POISONING - SOURCES

- **PRIMARY FUEL:** usually small deactivation compared to primary mechanism of arsenic poisoning or calcium sulfate masking
- **BIO-MASS:** vegetation can have large amounts of Na and K.
- **PROCESS SOURCES:** additives, etc.

*MBM – Meat and Bone Meal

PHOSPHORUS POISONING

SOURCES: Primary Fuel, Process Sources

Fuel Types

	hard coal	Lignite	sewage sludge	MBM	PRB coal (Wyodak)
Na as Na ₂ O [wt-%]	1.51	2.7	0.4	5.9	0.9
K as K ₂ O [wt-%]	2.91	1.6	0.7	2.75	0.7
P as P ₂ O ₅ [wt-%]	0.19	0.1	14.2	36.2	1.1

*MBM – Meat and Bone Meal

Reported Effects on SCR Activity during Co-Combustion

Coal + 4 wt-% Sewage Sludge

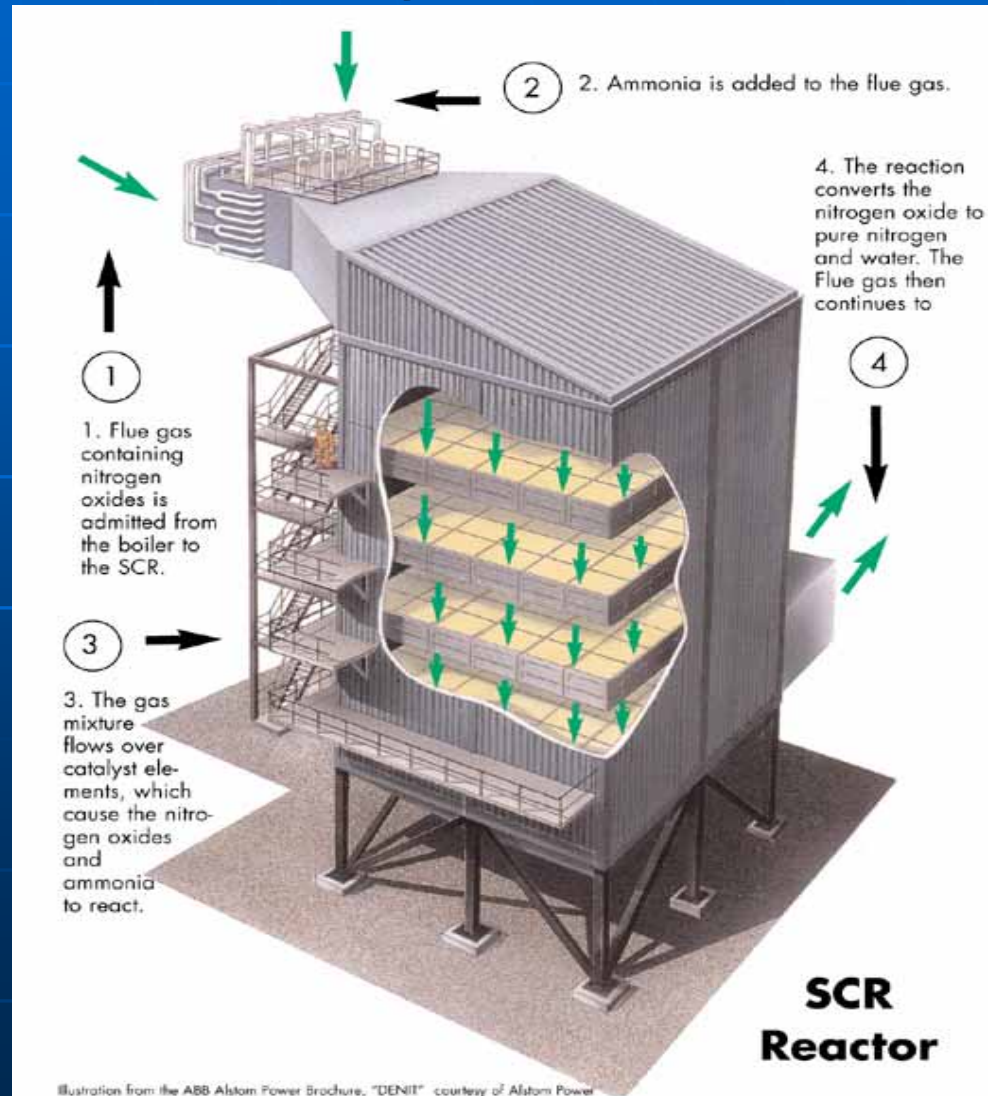
Higher deactivation
High P surface concentrations
(up to 4 wt-%)

Coal + 4 wt-% MBM

Rapid decrease in activity
(30 % in 4000 h)
High P surface concentrations
(up to 5 wt-%)
High amount of Na (bulk and surface)
Reduced surface area

*MBM – Meat and Bone Meal

UPDATE: Mercury Oxidation Across SCR Catalysts



SCR – Mercury Behavior Details

- Provides more residence time
- SCR catalyst are known to promote the oxidation of mercury
- Oxidation characteristics poorly understood
- Dependent on catalyst specifics, also time, temperature, ammonia, etc. ???
- Heavily influenced by flue gas constituents, especially chlorine

CATALYST DEVELOPMENTS FOR MERCURY CONTROL

- Better understand details of mercury chemistry and catalyst behavior
- Develop predictive methods for mercury oxidation behavior
- Improve Hg oxidation
- Maintain oxidation ability throughout life
- Offer guarantees for Hg oxidation

REFERENCES

1. "Deactivation of SCR Catalysts," Guo, X., et.al., ACERC Conference, February 17, 2005, Provo, UT.
2. "Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers, Pritchard, S., Cormetech, Inc.
3. "Deactivation Mechanisms of SCR Catalysts During the Co-Combustion of Bio-Residues," Beck, K., Universitat Stuttgart.

QUESTIONS ???