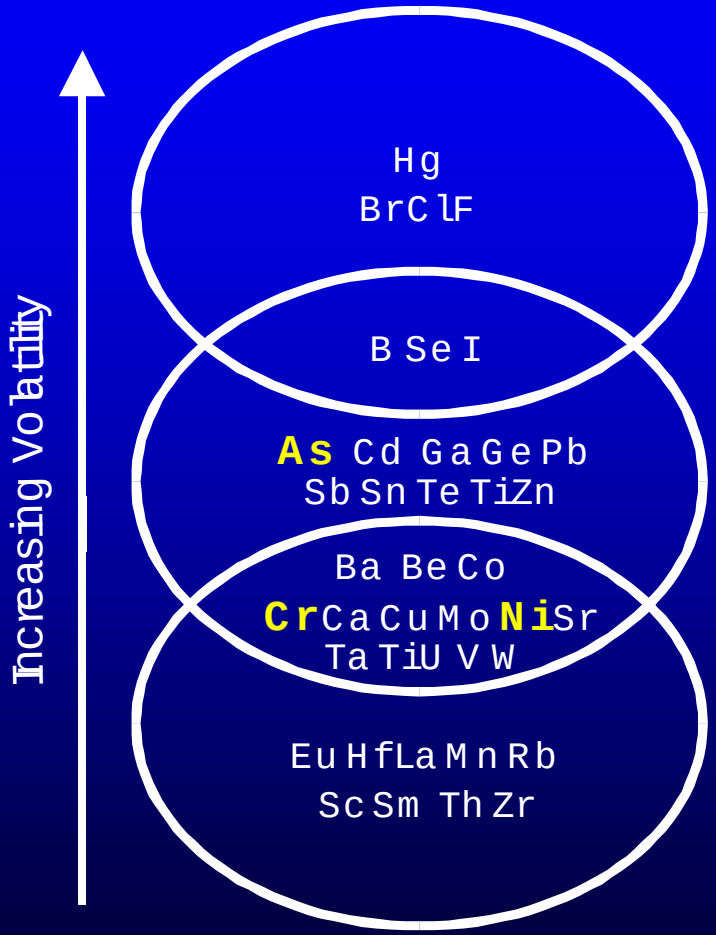
Formation and Speciation of Arsenic-, Chromium-, and Nickel-Bearing $PM_{2.5}$ Produced in a 7-kW Coal Combustion System

Kevin C. Galbreath
Christopher J. Zygarlicke
Energy & Environmental Research Center
University of North Dakota

Background

- As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, and U are among the 189 HAPs identified in the 1990 CAAA.
- As, Cr, and Ni pose the greatest inhalation health risk, primarily because of their known carcinogenic and toxicogenic potencies when in a As^{3+}, Cr^{6+}, and sulfidic Ni (*e.g.*, NiS_2 NiS, Ni_3S_2) form.

Trace Element Volatility Classification



Class III (volatile)
Volatilized and Emitted
as a Vapor

Class II (semivolatile)
Enriched in Fly Ash
and Depleted in Bottom Ash

Class I (nonvolatile)
Equally Distributed
Between Bottom Ash
and Fly Ash

Objective

- Evaluate the effects of trace element modes of occurrence and combustion conditions on As, Cr, and Ni volatility and speciation.

Experimental

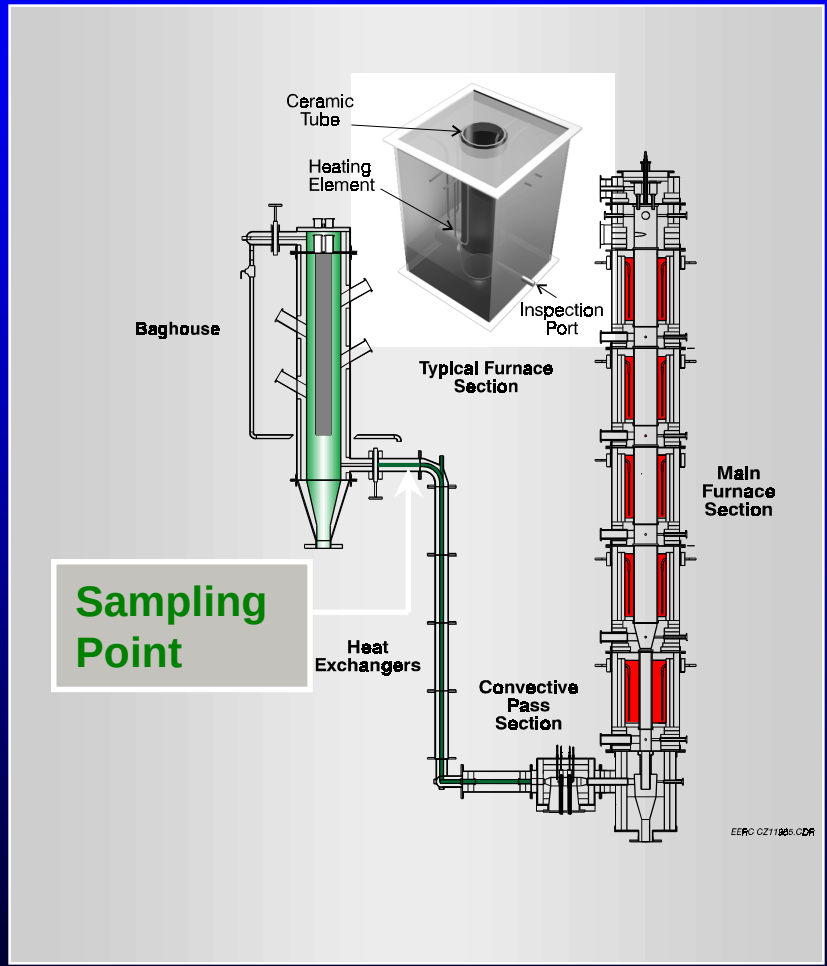
- Test coals
  - Bituminous Illinois No. 6 (Herrin)
  - Subbituminous Absaloka (Rosebud or McKay seam)
- Coal trace element modes of occurrence
  - Density separation
  - CCSEM and electron microprobe
  - Published XAFS results

Experimental (continued)

- 7-kW downfired combustion system
  - Conventional combustion
  - Low-NO_x combustion
- Fly ash and flue gas sampling
  - Five-stage cascade cyclone connected in series with an EPA Method 29 sampling train.

7-kW Combustion System

- 4.4 lb/hr (2 kg/hr) pulverized coal
- Preheat air 950°C
- Main furnace flue gas <1600°C
- Convective section 760°–1200°C
- 8 scfm (14 m^3/min) flue gas flow



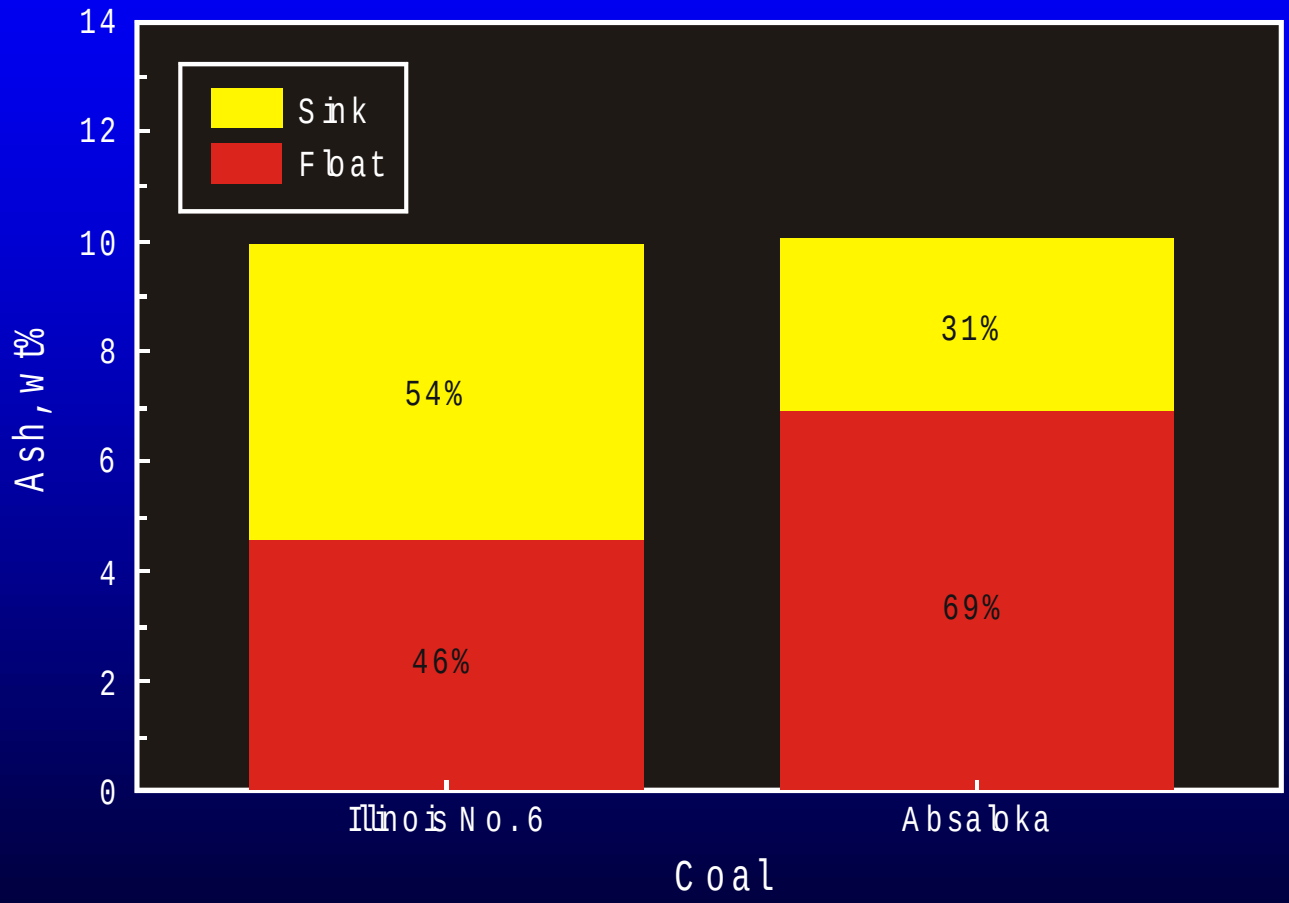
Experimental (continued)

- Trace element analysis
  - Microwave digestion (EPA Method 3050 and ASTM Method D3683)
  - GF-AAS or ICP-AES (EPA Methods 249.2 and 6010)
- $PM_{2.5}$ characterization
  - XRD
  - XAFS

Coal Trace Element Compositions

Element (ppm, moisture-free)	Illinois No. 6	Absaloka
As	2.1 (±0.1)	1.6 (±0.9)
Cr	20 (±1)	11 (±3)
Ni	11 (±0)	4.1 (±0.2)

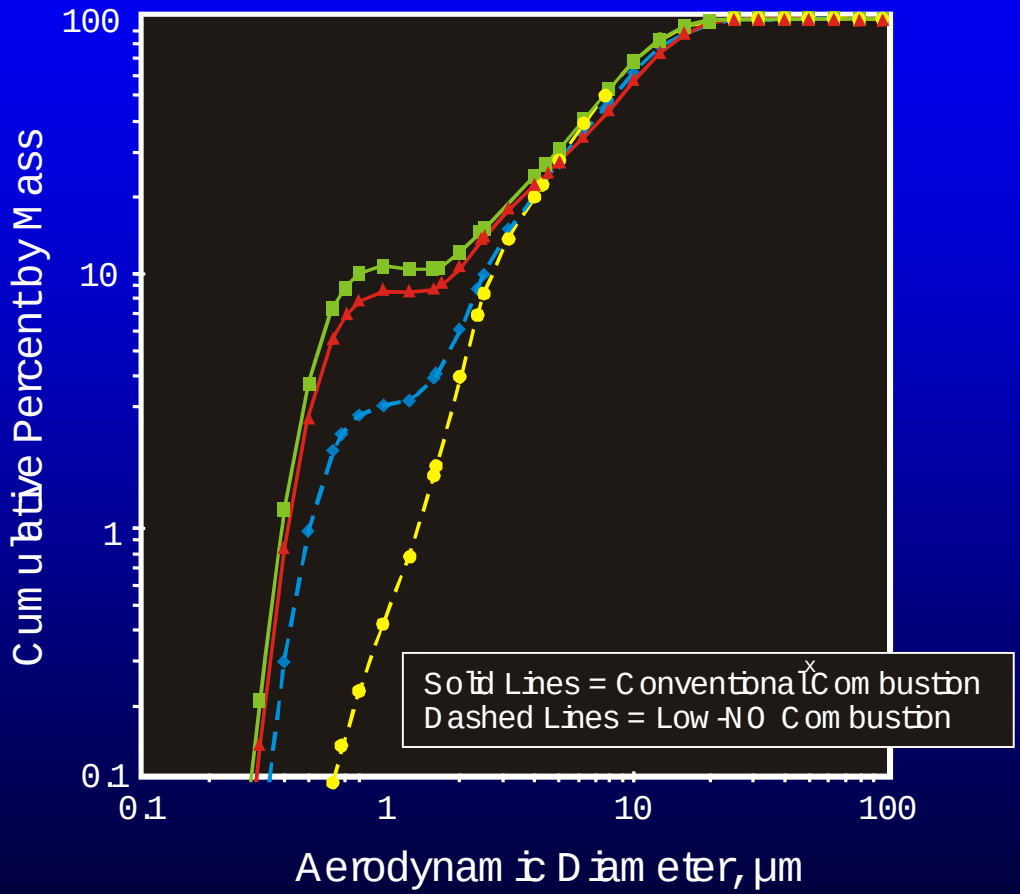
Density Separation Analysis Results



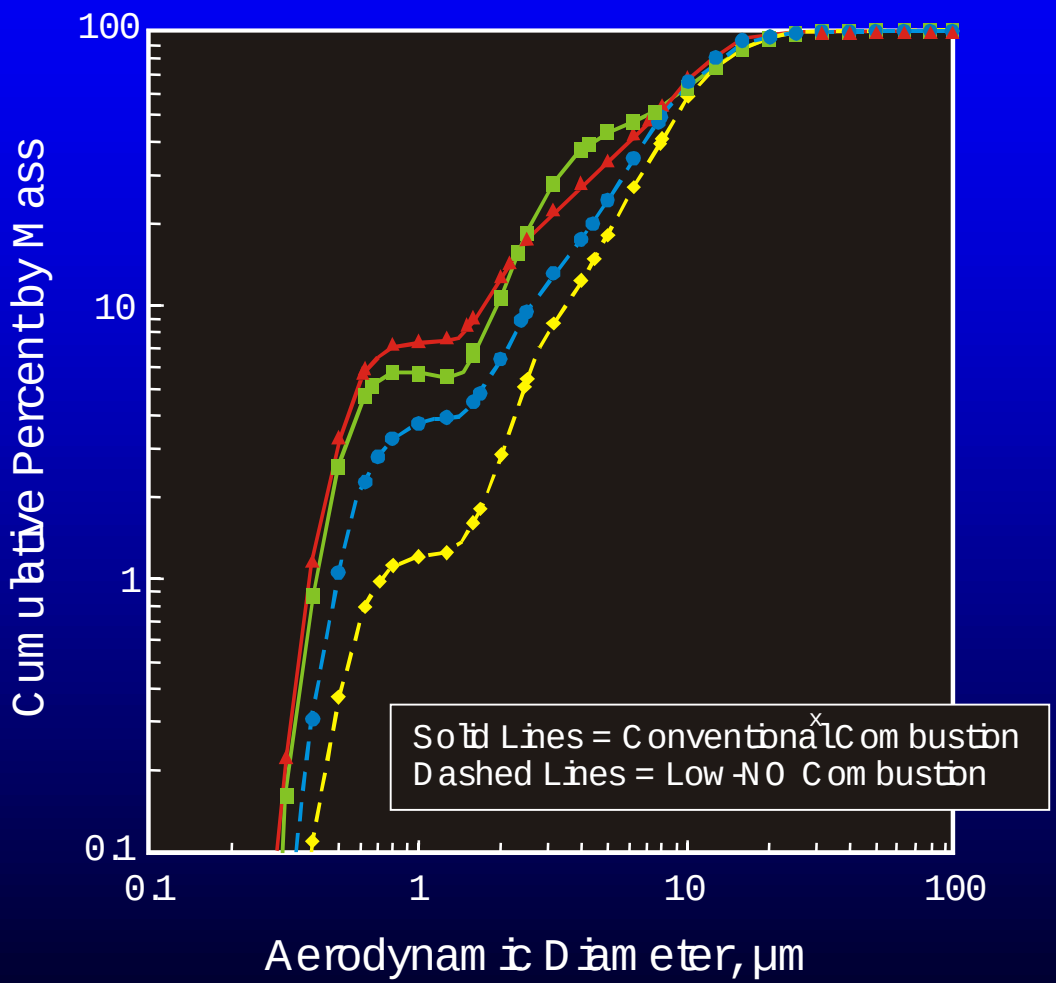
Dominant Trace Element Modes of Occurrence

Element	Illinois No. 6	Absaloka
As	Pyrite	Pyrite and maceral
Cr	Maceral (CrO[OH]) and illite	Maceral
Ni	Pyrite	Maceral

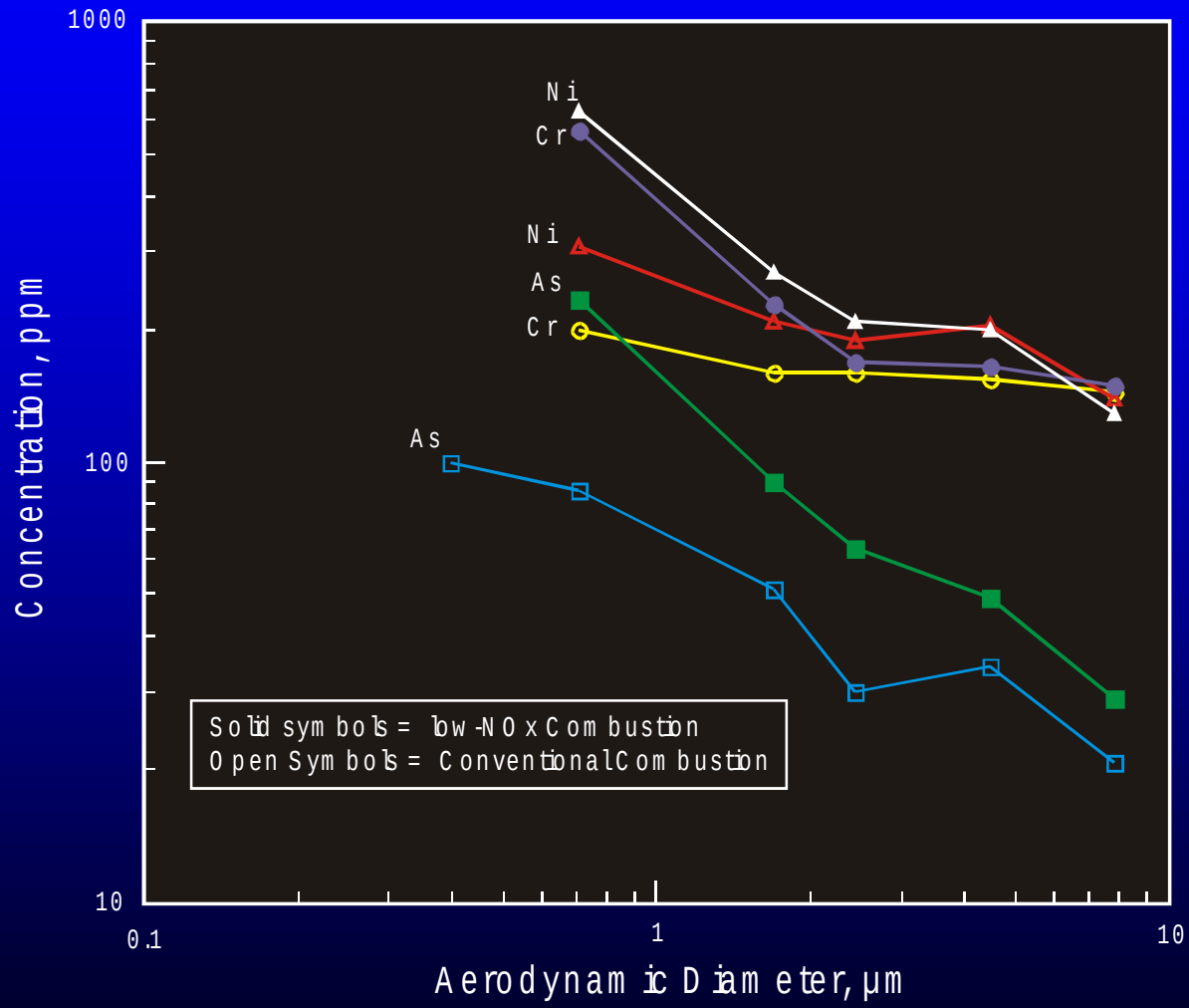
Illinois No. 6 Fly Ash PSDs



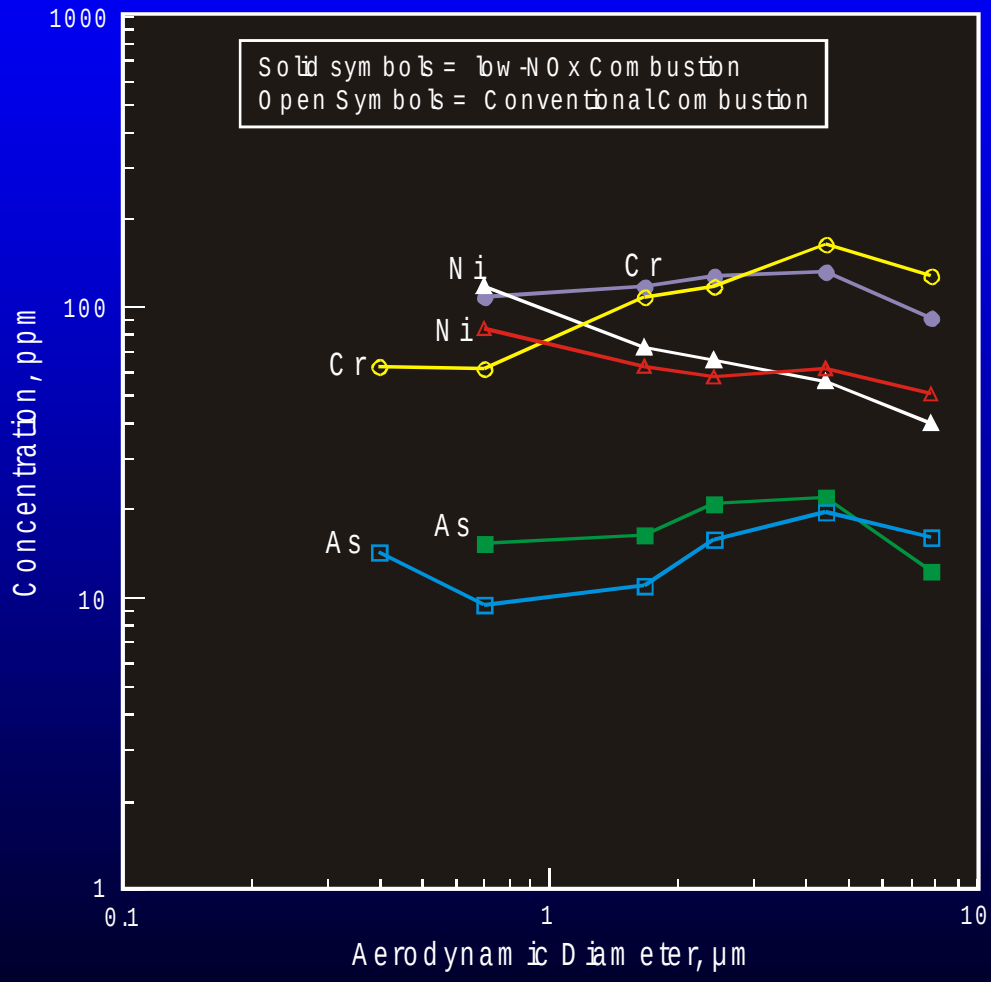
Absaloka Fly Ash PSDs



Illinois No. 6 Fly Ash As, Cr, and Ni PSDs



Absaloka Fly Ash As, Cr, and Ni PSDs



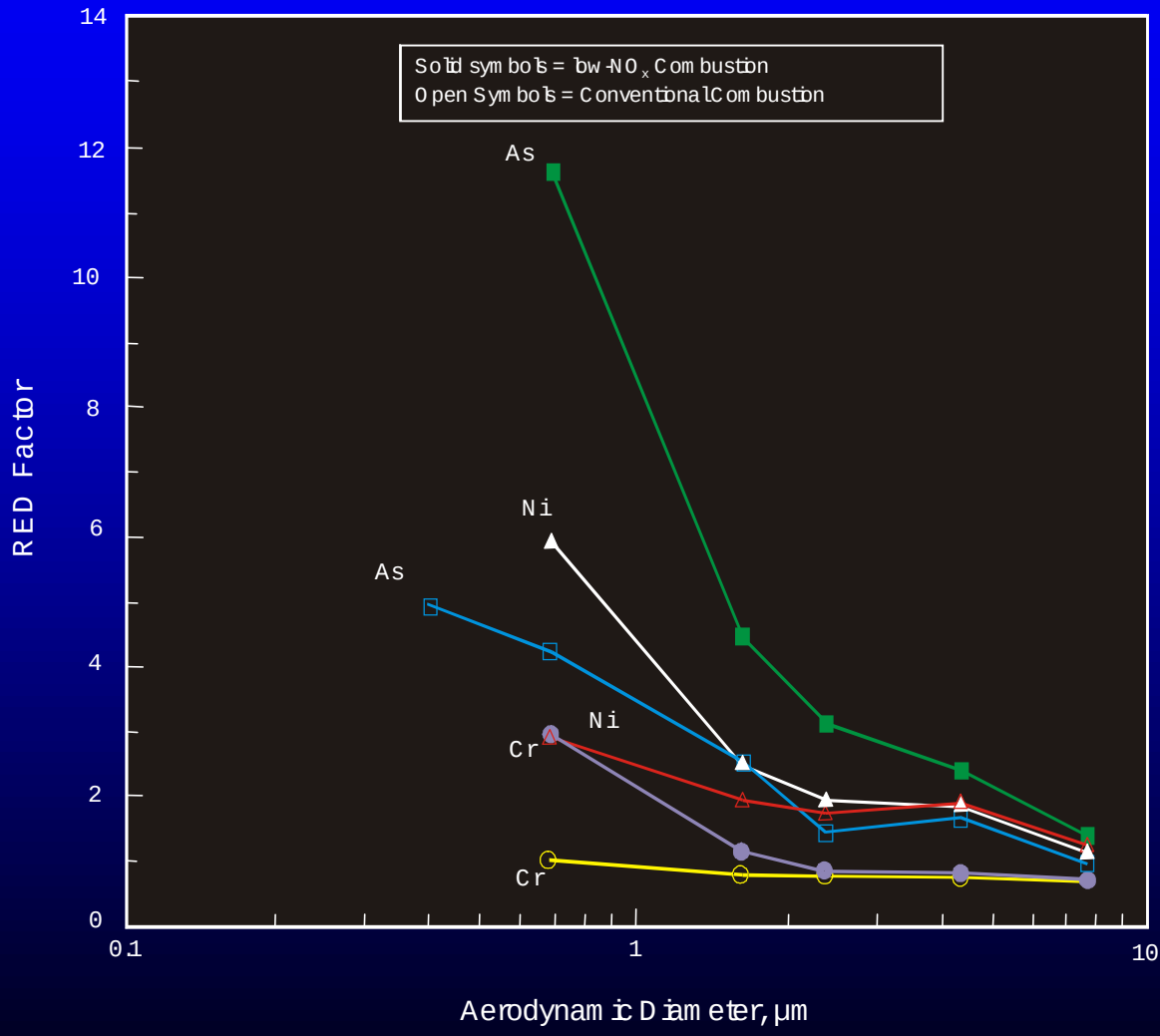
Evaluation of Trace Element (TE) Volatility

- TE relative enrichment/depletion (RED) factor

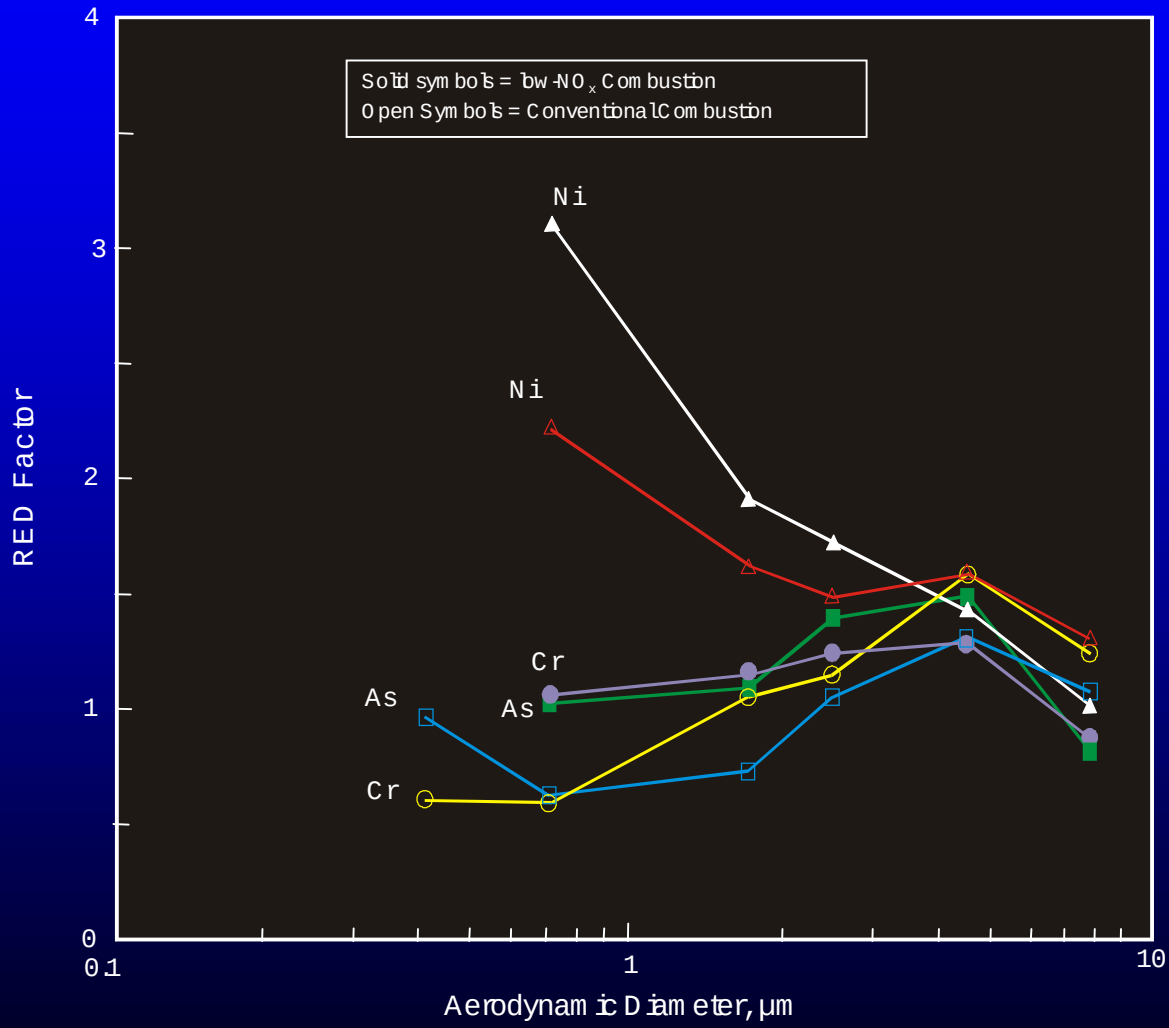
$$\text{RED factor} = \frac{\text{TE conc. in fly ash} \times \text{coal ash fraction}}{\text{TE conc. in coal}}$$

- Volatile TE
  - RED factors <<1
- Semivolatile TE
  - RED factor increases with decreasing particle size
- Nonvolatile TE
  - Consistent RED factors

Illinois No. 6 Fly Ash Trace Element RED Factors vs. d_{50}



Absaloka Fly Ash Trace Element RED Factors vs. d_{50}



Summary of As, Cr, and Ni Volatility

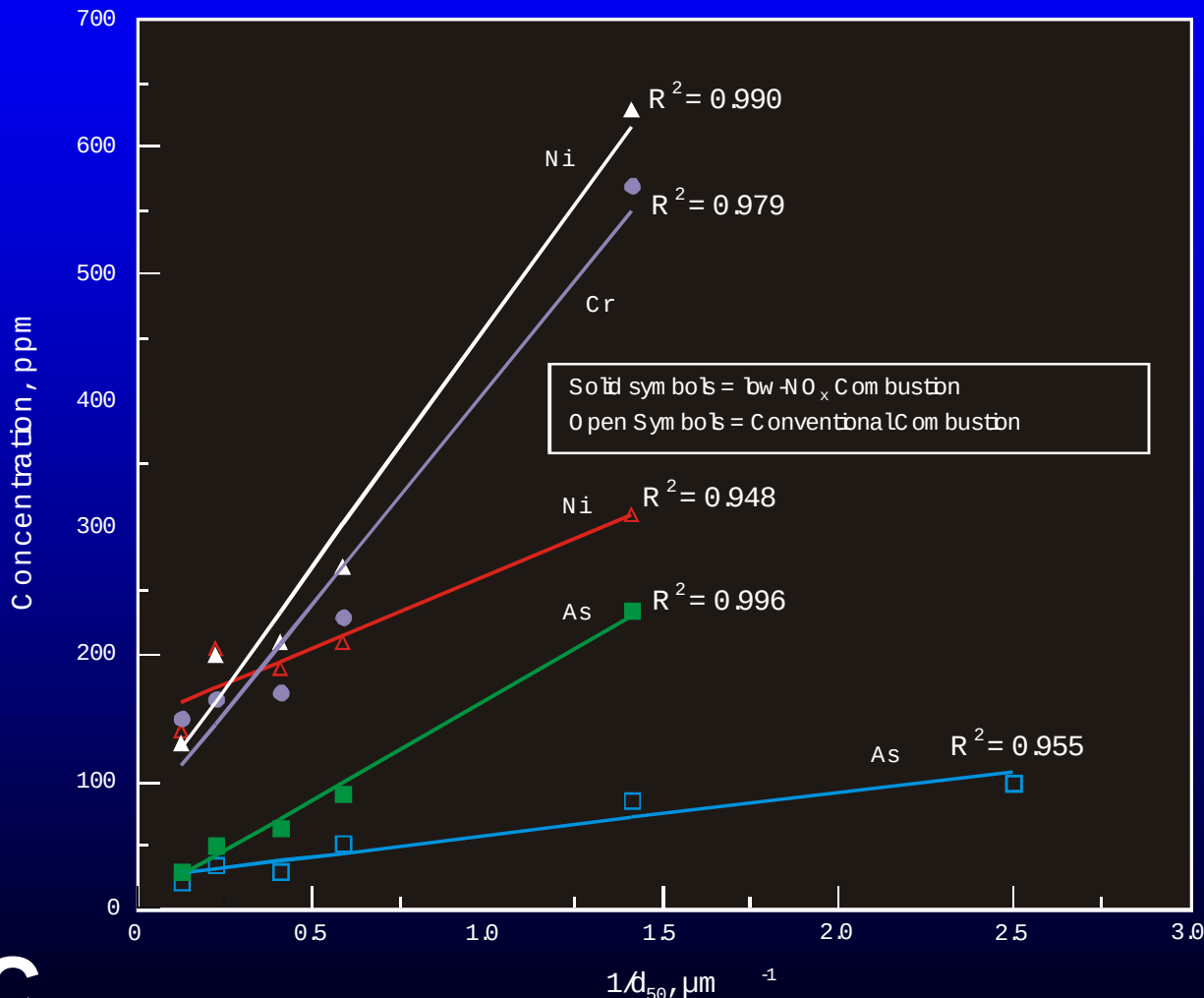
Coal	Nonvolatile	Semivolatile
Illinois No. 6	Cr[a]	As, Cr[b], and Ni
Absaloka	As and Cr	Ni

[a] Conventional combustion.
[b] Low-NO_x combustion.

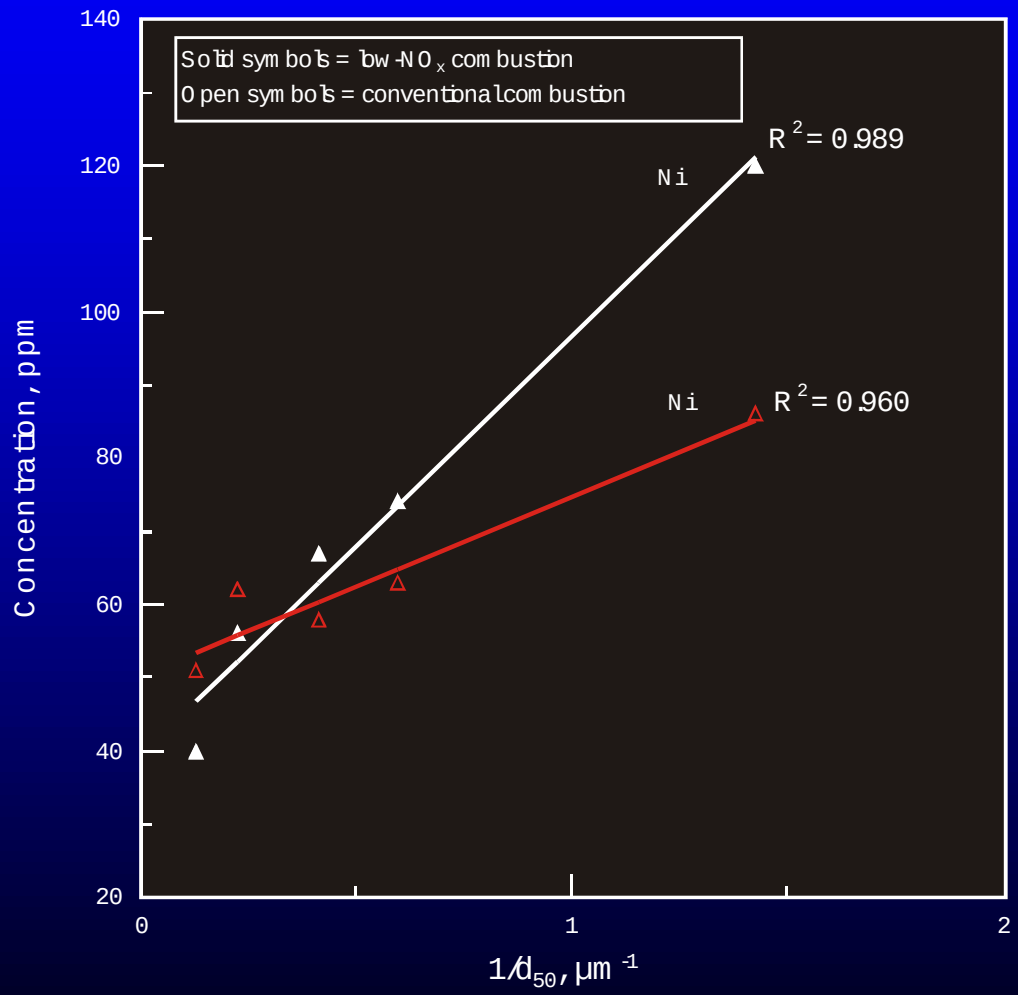
Semivolatile Trace Element Deposition Models

- Surface chemical reaction- and/or pore diffusion-controlled deposition process
  - Trace element concentration–PSD trend is proportional to $1/d_p$ (Davison et al., 1974)
- Physical condensation- and/or film diffusion reaction-controlled deposition process
  - Trace element concentration–PSD trend is proportional to $1/d_p^2$ (Flagan and Friedlander, 1978)

Illinois No. 6 Fly Ash Trace Element Concentrations vs. $1/d_{50}$



Absaloka Fly Ash Nickel Concentrations vs. $1/d_{50}$

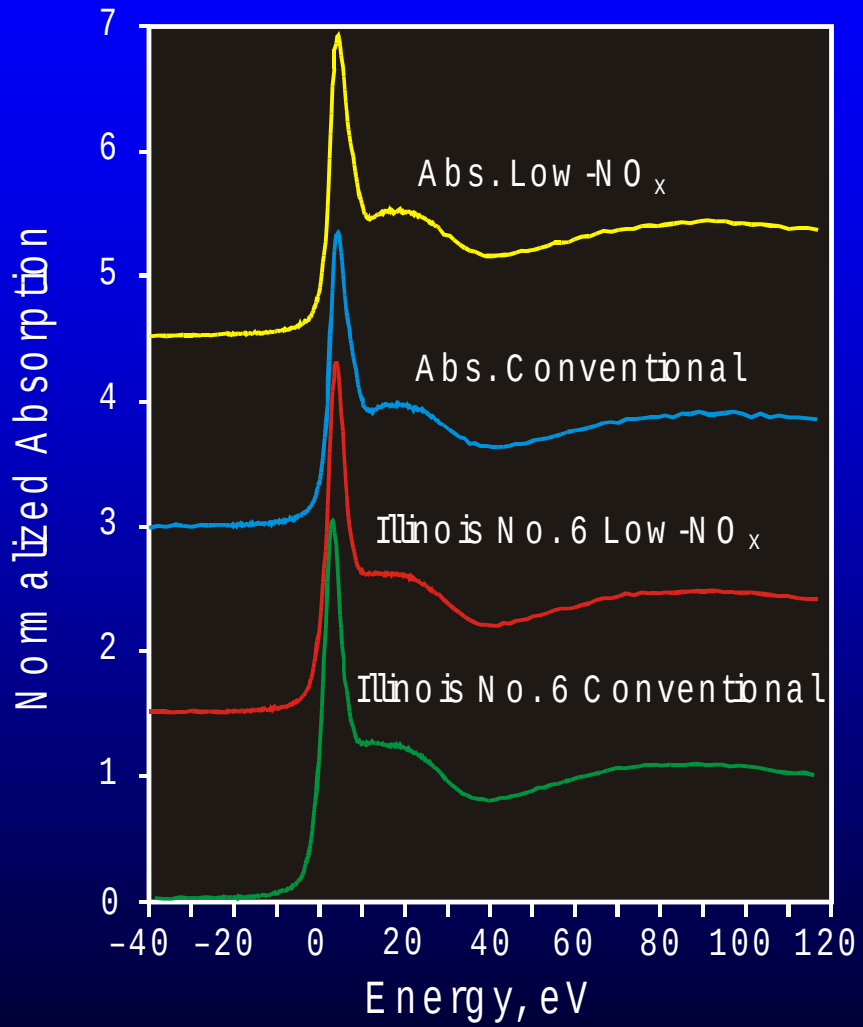


$PM_{2.5}$ Inorganic Phase Compositions

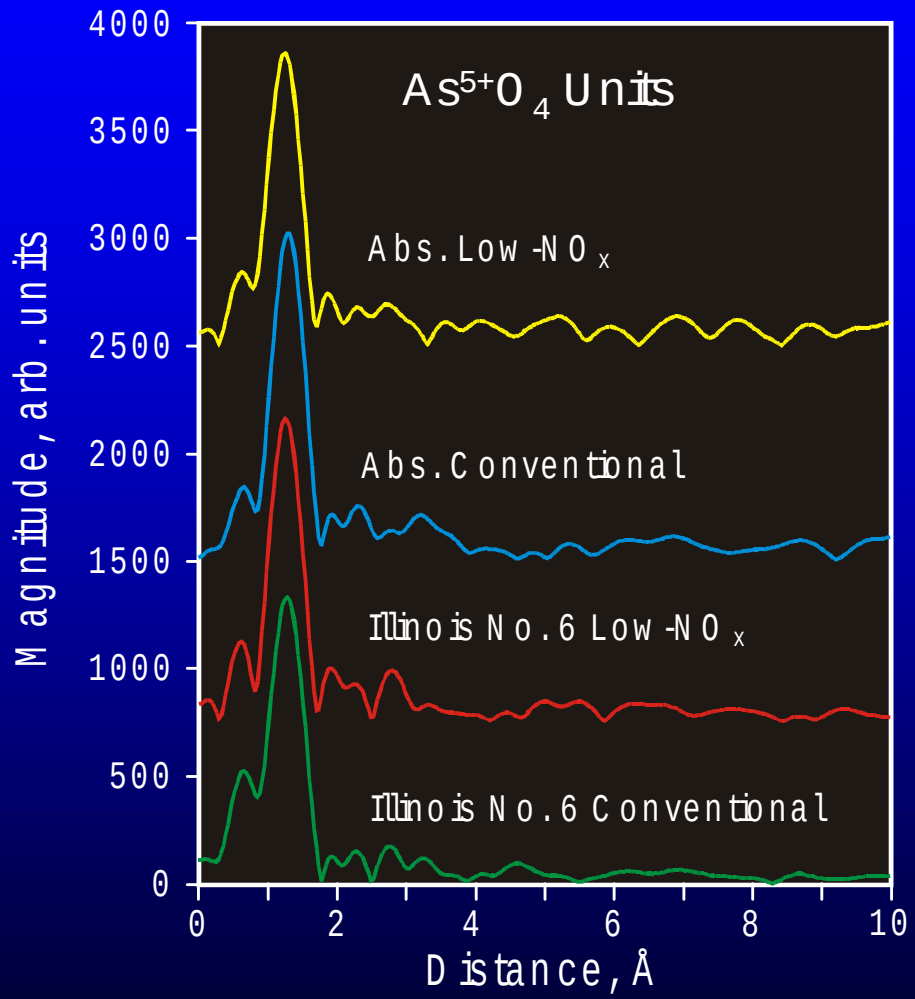
Phase, formula	Illinois No. 6	Absaloka
Glass	X	X
Quartz, SiO_2	X	X
Ferrite spinel,[a] AB_2O_4	X	X
Mullite, $Al_6Si_2O_{13}$	X	X
Anhydrite, $CaSO_4$	X	X
Lime, CaO		X
Periclase, MgO		X

[a] For example, where A^{2+} = Fe, Mg, Cu, Ni and B^{3+} = Al, Fe, Cr

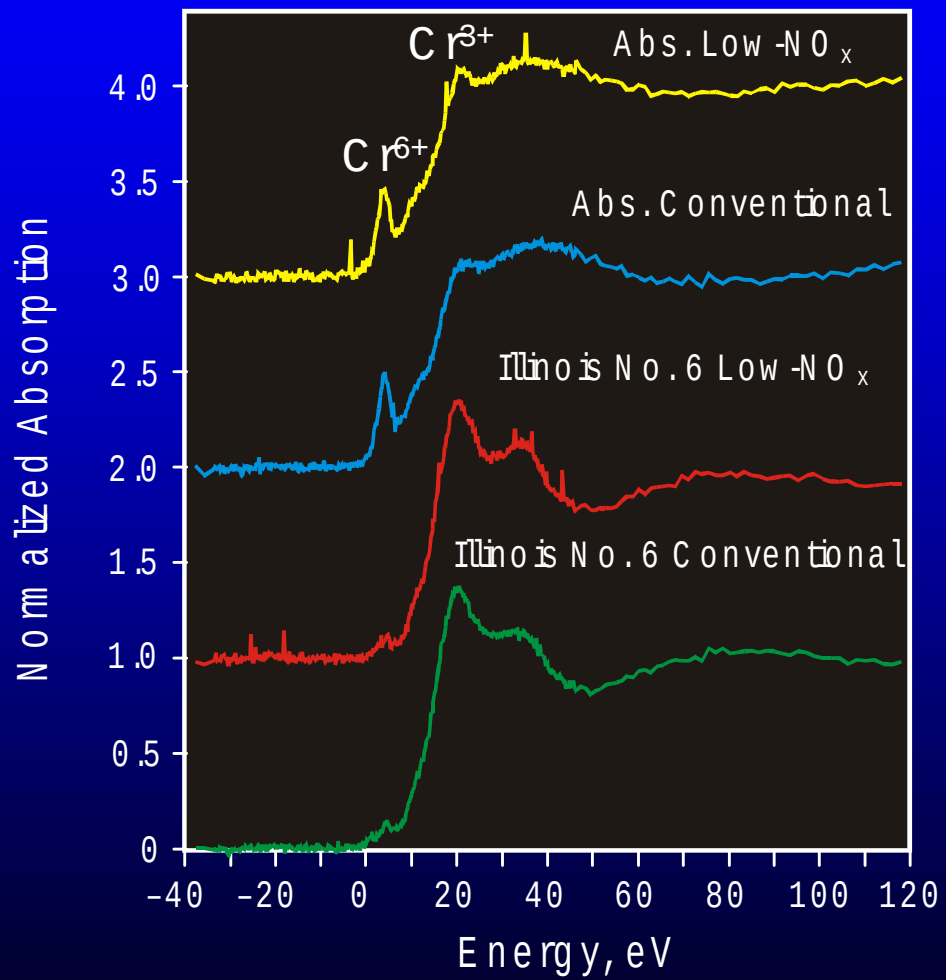
As K-edge XANES Spectra for $PM_{2.5}$



As RSF Spectra for $PM_{2.5}$



Cr K-edge XANES Spectra for $PM_{2.5}$



Summary of As, Cr, and Ni Speciation Results

Coal	As	Cr	Ni
Illinois No. 6	$As^{5+}O_4$	~94% Cr^{3+}, ~6% Cr^{6+}	$Ni^{2+}O$
Absaloka	$As^{5+}O_4$[a]	~57% Cr^{3+}, ~43% Cr^{6+}	$Ni^{2+}O$

[a] Possibly as $Ca_3(AsO_4)_2$.

Conclusions

- As, Cr, and Ni in the Illinois No. 6 coal are generally associated with relatively large discrete mineral grains, whereas in Absaloka coal they are much more strongly associated with macerals and fine-grained minerals.
- As, Cr, and Ni concentrations and RED factors for the Illinois No. 6 fly ashes generally increased with decreasing particle size which is consistent with an elemental vaporization–particle surface deposition process.
- As and Cr in Absaloka fly ashes were characterized by relatively uniform PSDs and RED factor–PSD trends which is indicative of nonvolatility.

Conclusions (continued)

- Low-NO_x Illinois No. 6 combustion promoted As, Cr, and Ni volatilization–particle surface deposition.
- Low-NO_x Absaloka coal combustion promoted Ni volatilization–particle surface deposition.
- Aluminosilicate glass, ferrite spinel, and mullite may be useful tracers for primary $PM_{2.5}$ from coal combustion.
- Combustion conditions did not significantly affect As, Cr, or Ni speciation.
- $As^{5+}O$- and $Ni^{2+}O$-containing phases occur in Illinois No. 6 and Absaloka $PM_{2.5}$.
- Cr^{3+}/Cr^{6+} is much greater in Illinois No. 6 $PM_{2.5}$, relative to Absaloka $PM_{2.5}$.