SPECIATION OF As, Cr and Ni IN CANADIAN FEED-COALS and COMBUSTION BY-PRODUCTS

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Introduction

- The toxicity of many trace metals towards humans is highly dependent on their speciation
  - As(III) is many (up to 50) times more toxic than As(V)
  - Cr(III) relatively harmless; Cr(VI) toxic and mutagenic
  - Ni subsulfides may be carcinogenic
- Oxidation state is also significant for:
  - Understanding the volatility and behavior of trace metals during combustion.
  - Leachability and mobility in ash-disposal situations.
- Speciation must be determined for coal and coal combustion products, especially in coal refuse and ash disposal situations.

IEA Round Robin: Speciation of Trace Elements in Coal

- International effort to assess current status of speciation of trace elements in coal
  - 1997-1999 Experimental phase
  - 4 coals: Australian, UK, USA and Canada
  - 7 groups participated:
    - » Selective leaching/element analysis (4)
    - » Float-Sink/SEM/Element analysis (1)
    - » Both Float-sink and leaching/element analysis (1)
    - » Float-Sink/XAFS spectroscopy (1)
- Results issued as an IEA Report (2000)

IEA Round Robin: Speciation of Trace Elements in Coal

- Be, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, Sb, Hg and Pb
- Methods agreement was:
  - Consistent for As, Se, Pb
  - Poor for Be, Co, Ni and Sb
- Indirect methods can only confirm what is known about speciation
  - Incapable of identifying new forms
- Emphasized need for direct methods
  - Electron microscopy/microprobe methods
  - XAFS spectroscopy

Objectives of current study

- Identify species of As, Cr and Ni in the feed coals and ash by-products from seven Canadian power plants (including one with a fluidized-bed combustor).
- Provide better understanding of the human health and environmental problems posed by these elements as a result of coal combustion

Methodology

- Feed coal, bottom ash, ESP ash and stack ash were sampled on three consecutive days following EPRI recommendation
- Standard analysis methods:
  - Total, pyritic, and sulphate sulphur (ASTM)
  - Trace metals by hydride AAS, INAA, ICP-MS, etc.
  - Enrichment indices by Meij's method.
- Speciation analysis methods:
  - XAFS Spectroscopy
  - SEM, XRD, XPS

Samples

- Seven Power Plants
  - 6 conventional pc-fired; 7th fluidized-bed combuster
- 4 Subbituminous Coals and 3 Bituminous Coals
  - 4 sbb coals and 1 bit. coal from Alberta
  - 2 bit. coals from Nova Scotia
- Power Plant Ashes
  - Bottom Ashes
  - Electrostatic Precipitator (ESP) Fly Ashes

Total sulphur and sulphur forms (%), trace metal contents (mg/kg) of subbituminous and bituminous feed coal.

Coal Rank	Subbituminous				Bituminous		
Stations	1	2	3	4	5	6	7**
Depositional Environment	Fresh Water		Brackish		Fresh Water		
Boron Content (mg/kg)	69	49	217	266	57	16	21
Sulphur Forms and Total Sulphur							
%Total Sulphur	0.24	0.22	0.38	0.54	0.46	2.6	3.56
%Sulphatic	0.01	0.01	0.01	0.1	0.06	0.1	0.13
%Pyritic	0.04	0.03	0.05	0.01	0.08	1.9	2.65
Organic by difference	0.19	0.19	0.32	0.43	0.32	0.6	0.78
Total Arsenic (mg/kg)	1.6	2.2	1.8	3.6	4.4	54	84
Chromium (mg/kg)	12	6	4.5	29	52	5	10
Nickel (mg/kg)	6.3	4.3	5.3	5.7	15	8	14

*After Goodarzi and Swaine 1994 **Fluidized bed combustion

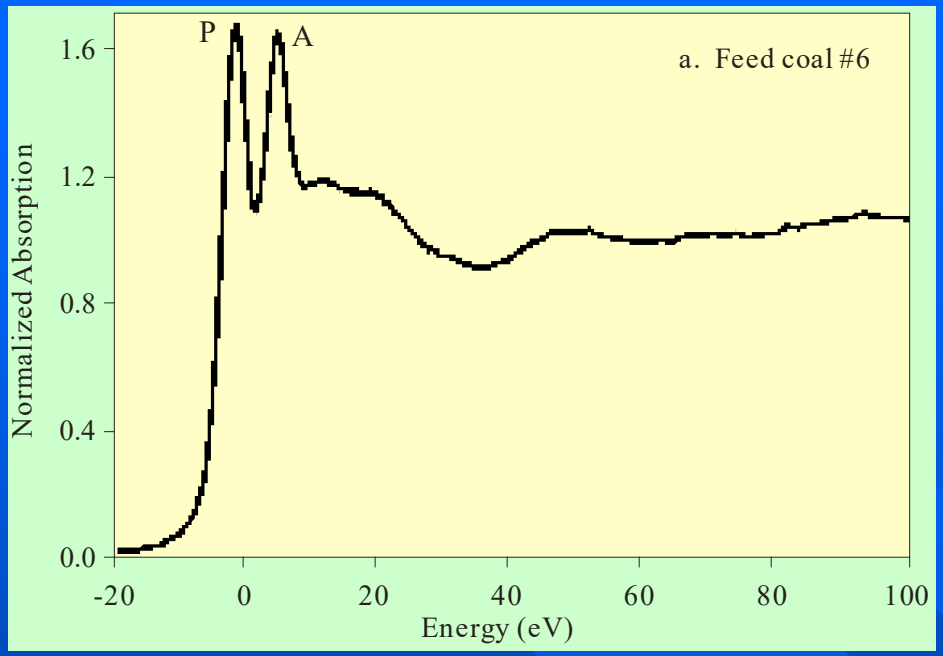
XAFS Methodology

X-ray Absorption Fine Structure (XAFS) Spectroscopy:

- Synchrotron-based method
  - Stanford Synchrotron Radiation Laboratory (SSRL)
  - National Synchrotron Light Source (NSLS)
- The XAFS spectra were collected in fluorescence geometry using a 13-channel germanium detector
  - Each channel gated to receive only K_α X-rays of element of interest
- XAFS spectra – two regions of interest
  - XANES (X-ray absorption near-edge structure)
    - » Fingerprint; reflects local bonding to element of interest
  - EXAFS (extended X-ray absorption fine structure)
    - » Fourier transform to yield Radial Structure Function (RSF)
    - » Local structure surrounding element of interest

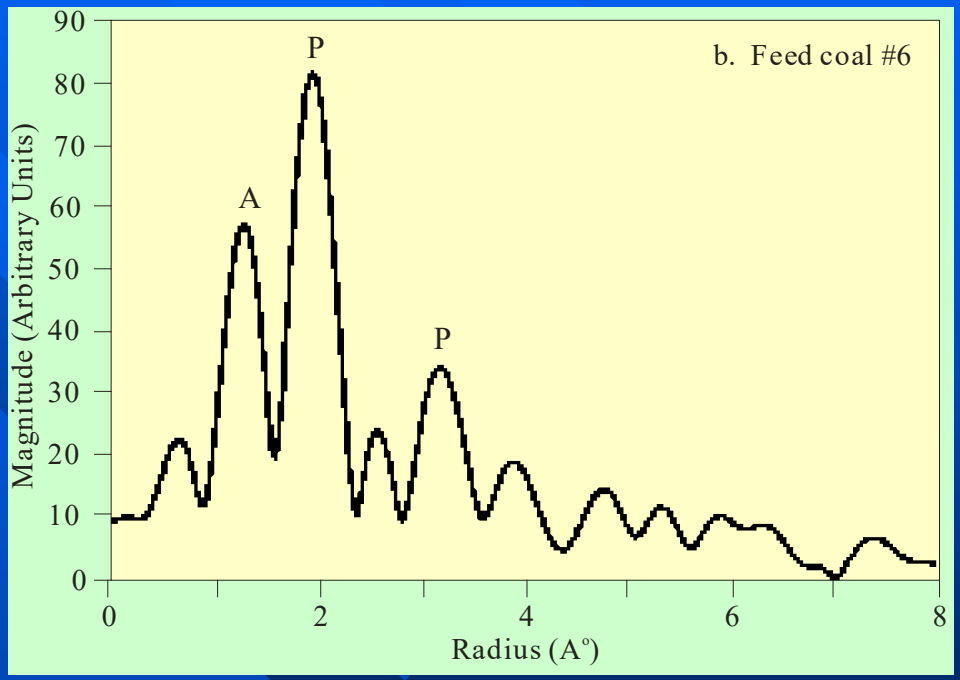
XAFS Spectroscopy

- Advantages:
  - Direct and non-destructive probe
  - Element-specific, little chance of interference
  - Material and state-of-matter independent
- Versatile:
  - Applicable to most elements
  - Concentration range from 1 ppm to 100%
  - Reflects both local structure and bonding
- Disadvantages:
  - Synchrotron source required
  - One element at a time

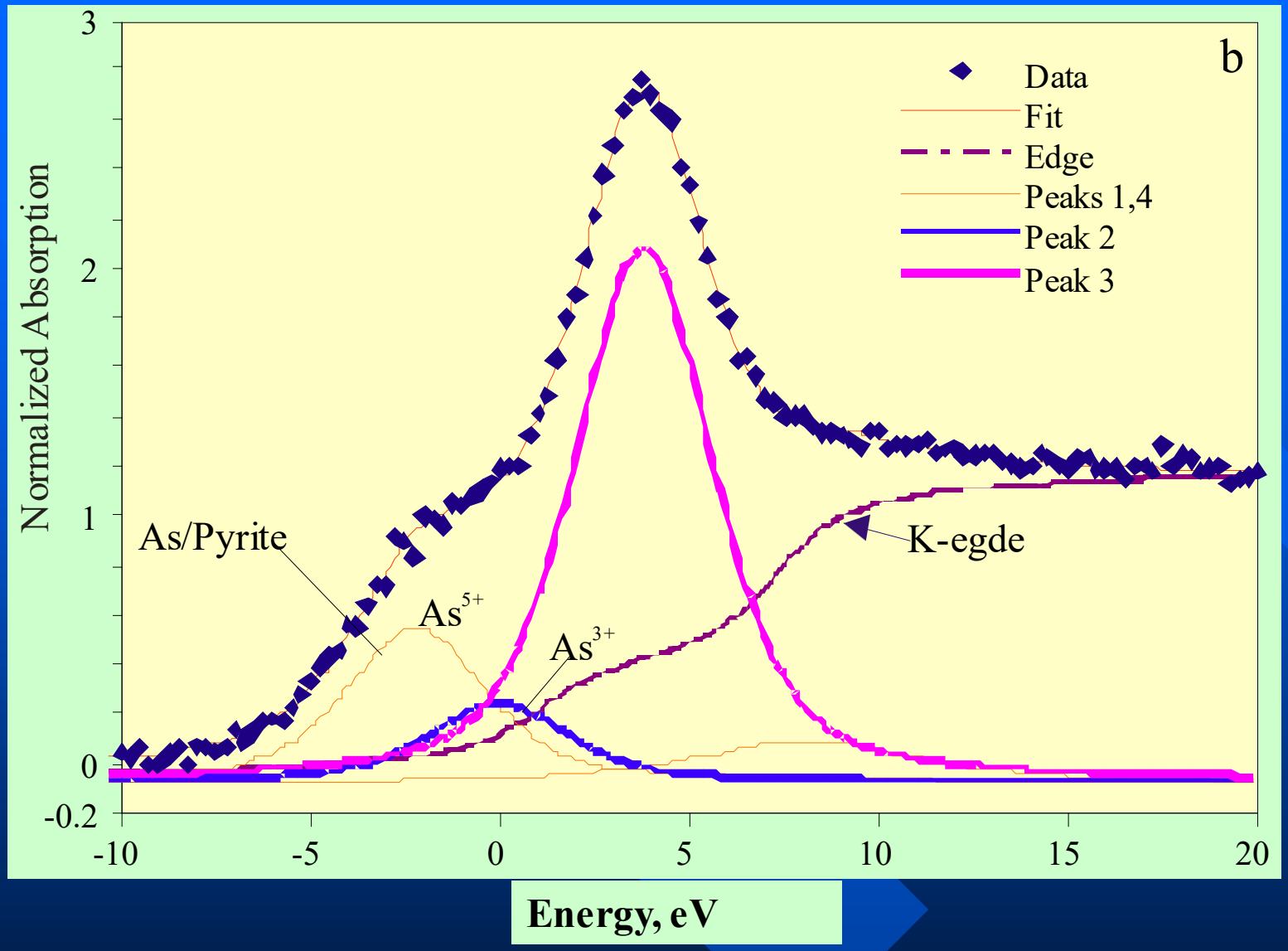


XANES

EXAFS/RSF



(a) Arsenic K-edge XANES spectra of high sulphur/pyrite bituminous coal #6. (b) Radial structure function (RSF) derived from the As EXAFS spectral region of high pyrite bituminous coal. Peaks denoted by "A" and "P" arise from As as arsenate and As in pyrite, respectively.



Least-squares fitted arsenic XANES spectrum of feed coal #5 showing deconvolution of the spectrum into component peaks.

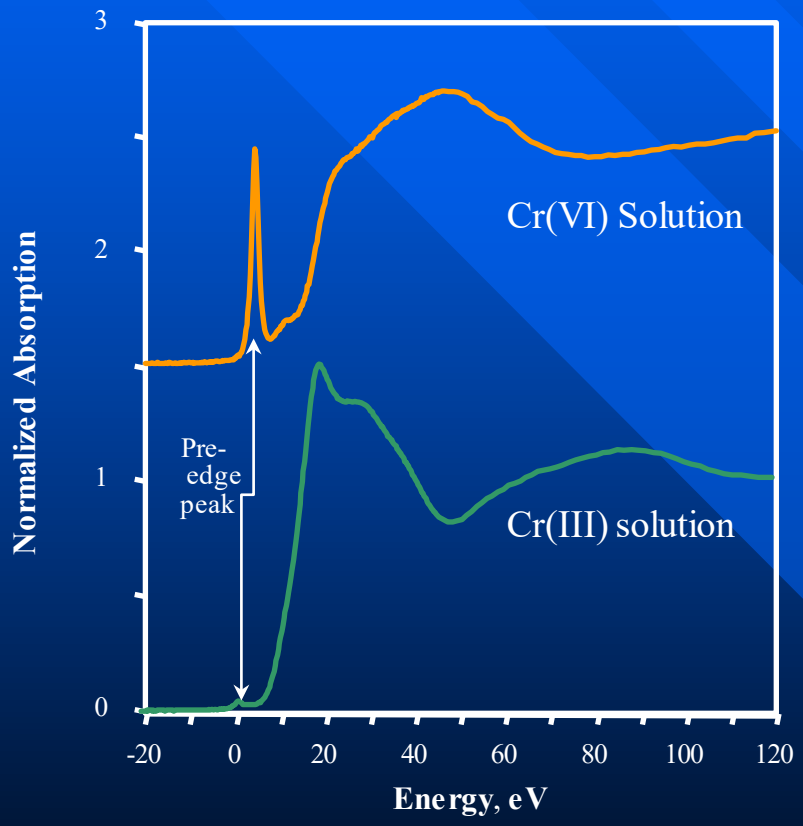
Summary of As, Cr, and Ni Oxidation States in Coals

Species (%)	Subbituminous				Bituminous		
	#1	#2	#3	#4	#5	#6	#7
As_2^{2-} (pyrite)	0	0	0	84	34	77	82
As^{3+} (organic)	50	50	50	7	12	0	0
As^{5+} (arsenate)	50	50	50	9	54	23	18
Cr^{3+} (clay/oxide)	100	100	100	100	100	100	~50
Cr^{0} (steel)	0	0	0	0	0	0	~50
Ni^{2+}	100	100	100	100	100	100	100

Summary of Findings - Arsenic

- Speciation of As in Canadian Coals
  - Western Canada
    - » As contents are low
    - » Main forms are organically-bound As(III) and arsenate
  - Eastern Canada
    - » Much higher As contents
    - » Main forms are As/Pyrite and arsenate
- Speciation of As in ash samples
  - As in fly ash and stack ash is >95% As(V)
  - Up to 20% of As as As(III) in bottom ash

Chromium Speciation Concerns



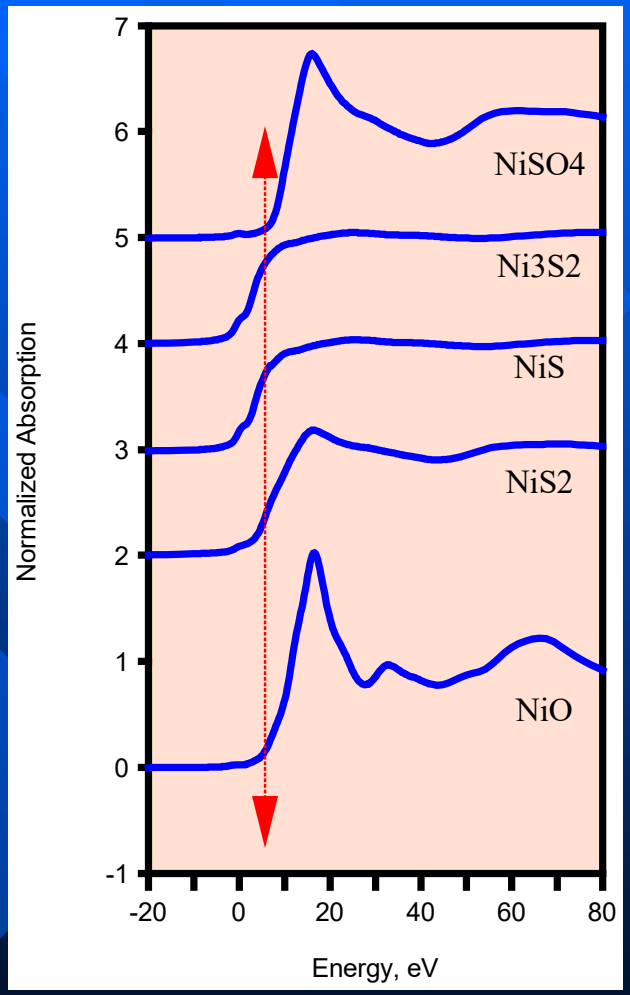
- Discrimination between oxidation states of Cr
  - Cr(III) not toxic at concentrations found in most coals and ash
  - Cr(VI) highly toxic and carcinogenic
- Readily differentiated by Cr XAFS Spectroscopy
  - Height of pre-edge peak
  - Shape of spectrum

Summary of Findings - Chromium

- Speciation of Cr in Canadian Coals
  - Western and Eastern Canada
  - Lower Cr contents in western coals
    - » Mostly Cr^{3+}/illite; some organically associated Cr(III)
    - » No evidence for Cr(VI) in any coal
    - » Metallic Cr as stainless steel observed in one coal
- Speciation of Cr in ash samples
  - Bottom ash: >90% Cr(III)
  - Fly-ash: mostly Cr(III), but some Cr(VI) observed
    - » Up to 15% Cr(VI) observed in fly-ash from western Canadian plants

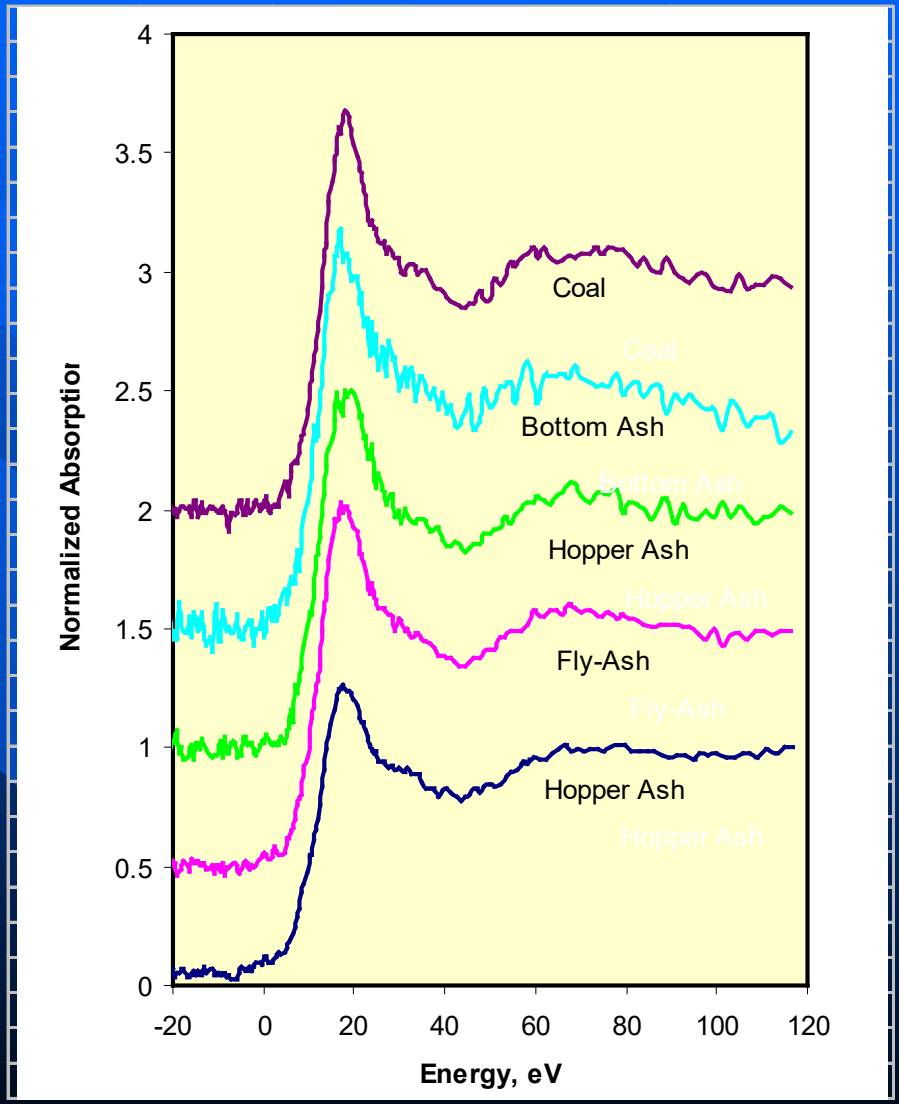
Nickel Speciation Concerns

- Health danger of Ni subsulfides (Ni_3S_2, etc.) is well established:
  - Carcinogenic and toxic
- Do Ni subsulfides exist in coal?
- Can Ni subsulfides be formed in ash products?
- Discrimination is possible using XAFS Spectroscopy
  - Spectral shape
  - Position of edge



Ni XANES - Canadian Coal and Ash Products

- Ni in coal
  - Exclusively Ni^{2+}
  - Ni distributed between oxide and sulphide forms
- Ni in ash
  - Predominantly Ni^{2+}
  - Ni-S phases absent



Summary of Findings - Nickel

- Speciation of Ni in Canadian Coals
  - Speciation in coal less certain than Cr or As
    - » Sulfide association in some coals
    - » Oxide association in other coals
- Speciation of Ni in ash samples
  - Ash: >90% Ni in oxidic forms
    - » Glass, sulfates, oxides
    - » No evidence for carcinogenic Ni-sulfides
- Needs more detailed study

Possible Future Collaboration

- Discussion of possible international study involving speciation and behavior of critical elements during combustion
  - Netherlands, Canada, USA
  - Combustion emissions are a worldwide problem
- Particulate Matter issues
  - Ultrafine (<1 micron) particulate matter
- Mercury emissions and control
  - Control by activated carbon sorbents

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