Fly Ash: From Cradle to Grave

Edited by Margaret S. Ellis and Ronald H. Affolter

Tutorial/Workshop, June 10, 2007, 12:15 p.m.-2:15 p.m.

32nd International Technical Conference on Coal Utilization & Fuel Systems
The Power of Coal
The Clearwater Coal Conference
June 10-15, 2007
Sheraton Sand Key, Clearwater, Florida, USA

U.S. Geological Survey Open-File Report 2007-1160

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia 2007

For product and ordering information:
World Wide Web: http://www.usgs.gov/pubprod
Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth,
its natural and living resources, natural hazards, and the environment:
World Wide Web: http://www.usgs.gov
Telephone: 1-888-ASK-USGS

Table of Contents

[1] U.S. Geological Survey, Denver, Colorado USA

[2] University of Kentucky, Lexington, Kentucky USA

Introduction

The principal mission of the U.S. Geological Survey (USGS) Energy Resources Program (ERP) is to (1) understand the processes critical to the formation, accumulation, occurrence, and alteration of geologically-based energy resources; (2) conduct scientifically robust assessments of those resources; and (3) study the impact of energy resource occurrence and (or) production and use on both environmental and human health. The ERP promotes and supports research resulting in original, geology-based, non-biased energy information products for policy and decision makers, land and resource managers, other federal and state agencies, the domestic energy industry, foreign governments, non-governmental groups, academia, and other scientists. Investigations include research on the geology of oil, gas, and coal and the impacts associated with energy resource occurrence, production, quality, and utilization. The ERP's main focus on coal is to support investigations into current issues pertaining to coal production, beneficiation and (or) conversion, and the environmental impact of the coal combustion process and coal combustion products (CCPs). To accomplish, the USGS combines its activities with other organizations, including donor organizations, to address domestic and international issues relating to the development and use of energy resources.

Coal quality, composition of stack emissions, and coal combustion products (CCPs) have become major environmental concerns as the rate of coal utilization increases nationally. With increasing emphasis on environmental issues, information on the quality of coal, which includes ash yield, sulfur content, and heat value, as well as major-, minor-, and trace-element content, has become as important as information on the quantity of the resource. Therefore, it is important to determine how these elements are distributed in the feed coal, the resulting changes in composition as coal is processed, and the chemical composition of the CCPs. Because (1) coal-quality data are important to the resource classification system (as applied by the USGS), and (2) utilization of coal may be regulated for its possible effect on the environment, any evaluation of future coal resource potential should therefore consider quality as well as quantity.

It is a widely accepted fact that the environmental "footprint" of coal utilization will have to continue to be reduced in the future. One of the basic building blocks to accomplish this goal is the development of sound databases that document the relation between geological controls on coal quality and the resultant CCPs. An integrated approach to coal quality work-- a "cradle to grave" approach-- focuses on more than one aspect of the coal, such as how and (or) where different coal quality characteristics form and what happens to them through the process of mining, production, transport, utilization, and waste disposal.

In order to determine these characteristics, an extensive suite of coal-quality analyses, mineralogical, petrology, and leaching investigations are performed on samples (both pre- and post-combustion) taken during different phases of the coal-utilization process. The feed coal, fly ash, and bottom ash sampling times are closely coordinated so that feed coal samples can be matched as closely as possible with the corresponding CCP samples. The goals of these types of study are to follow the flow of coal through the power plant, and finally to the disposal or utilization of the various CCPs. The results help to evaluate the relation of coal composition to the resultant CCPs, because the content, distribution, and behavior of elements during and after the combustion process depend in large part on the content and distribution of trace elements in the feed coal. With an adequate amount of data from these studies, general predictive models could be developed so that issues like ash disposal and CCP utilization are addressed with greater precision.

This type of research fosters a greater understanding of the fate and partitioning of elements during coal combustion, and leads to data that can be used to more accurately evaluate how coal-quality parameters affect air emissions and waste-disposal efforts. This tutorial will (1) examine how these studies are conducted under the Coal Quality and Utilization issues task and the importance of providing improved, comprehensive, science-based data sets that can be utilized by policy and decision makers; and (2) discuss the history of collecting quality USGS data on trace elements, laboratory methods and procedures, petrology, mineralogy, and leaching characteristics of CCPs.

Agenda

12:15 p.m.	Introduction, Project Summary, and Trace Elements—*By* Ronald H. Affolter
12:35 p.m.	Laboratory Setup, How Elements are Analyzed, and Quality Assurance/Quality Control (QA/QC)—*By* Jamey D. McCord
12:55 p.m.	Petrology of Feed Coal and Fly Ash—*By* James C. Hower
1:15 p.m.	Break
1:20 p.m.	Characterization of Feed Coal and Fly Ash Using X-Ray Diffraction and Microbeam Methods—*By* Michael E. Brownfield
1:40 p.m.	Leaching Studies by Batch, Sequential, Toxicity Characteristic Leaching Protocol (TCLP), and Synthetic Precipitation Leaching Protocol (SPLP)—*By* Cynthia A. Rice
2:00 p.m.	Questions and Answers—*By* Ronald H. Affolter

Tutorial

Introduction, Project Summary, and Trace Elements

Slide 1

USGS
science for a changing world

Introduction, Project Summary, and Trace Elements

By

Ronald H. Affolter

U.S. Geological Survey, Denver, Colorado

U.S. Department of the Interior
U.S. Geological Survey

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 2

Instructor

Ronald H. Affolter

Ron Affolter is a geologist with the U.S. Geological Survey who works on coal quality and database issues involving the characterization of the chemistry, mineralogy, and overall quality of U.S. and world coals.

Ron has been an integral member of several multidisciplinary research teams providing coal quality data and quantity interpretations for the Colorado Plateau and Illinois Basin coal Assessment projects. He is currently a task leader for both the Coal Quality: Geologic Controls and Utilization Issues task and the Laboratory Analytical Issues and Quality Databases task. He is also the supervisor for the U.S. Geological Survey’s Geochemical Laboratory in Denver, CO and 2nd Vice Chairman for the Coal Geology Division of the Geological Society of America (GSA).

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 3

- History of Collecting Coal Quality Data Within the U.S. Geological Survey
- U.S. Geological Survey Energy Resource Program (ERP) 5-Year Plan
- Coal Quality: Geologic Controls and Utilization Issues Task
- Trace Element Studies

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 4

History of Coal Quality

- Since 1970, the U.S. Geological Survey has pursued a program to evaluate the chemical composition of coals in the United States.
- Collection of samples involved a cooperative effort among many different State and Federal agencies, private corporations, mines, and utilities.
- Data consist of geologic, stratigraphic, and chemical information collected from drill holes, face channels, mine cuttings, power plants, and outcrop samples.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 5

- Documentation and chemical analyses for most coal samples processed during this program are available to the public in more than 2,000 reports listed in part by Finkelman and others, (1991); Affolter and Hatch, (1995); and Ellis (1995).
- These reports list location, depth, thickness, and the basic geology of the sampled coal beds and summarize proximate and ultimate analyses and major-, minor-, and trace-element composition of the coal samples.
- Bed summaries are also available on the COALQUAL Database CD-ROM (Bragg and others, 1997) and individual samples on the National Geochemical (PLUTO) Database (Baedecker and others, 1998).

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 6

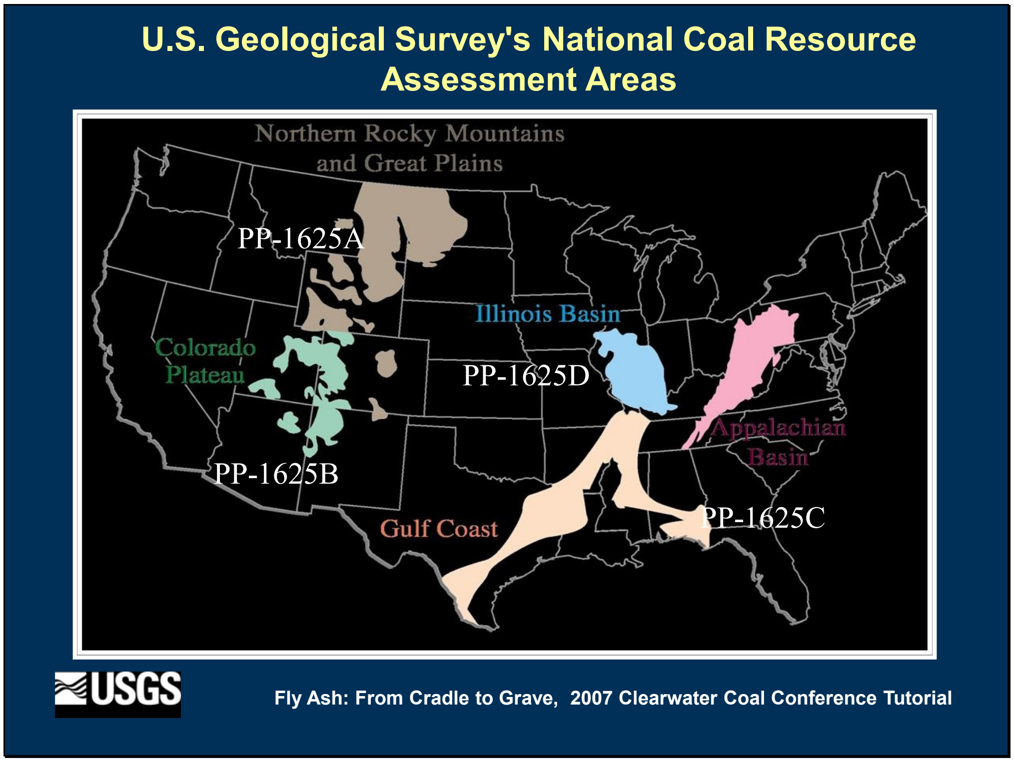
Coal Quality

Because coal quality data are essential components of the U.S. Geological Survey's resource classification system (Wood and others, 1983),
any evaluation of coal resource potential must consider quality as well as quantity.

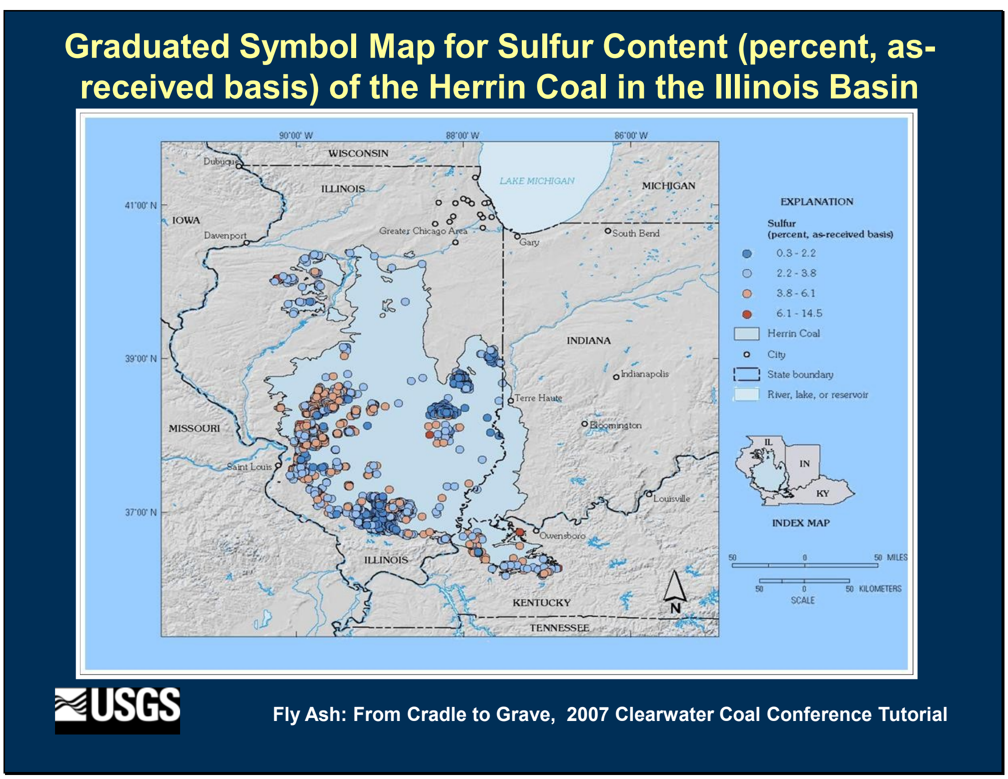
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

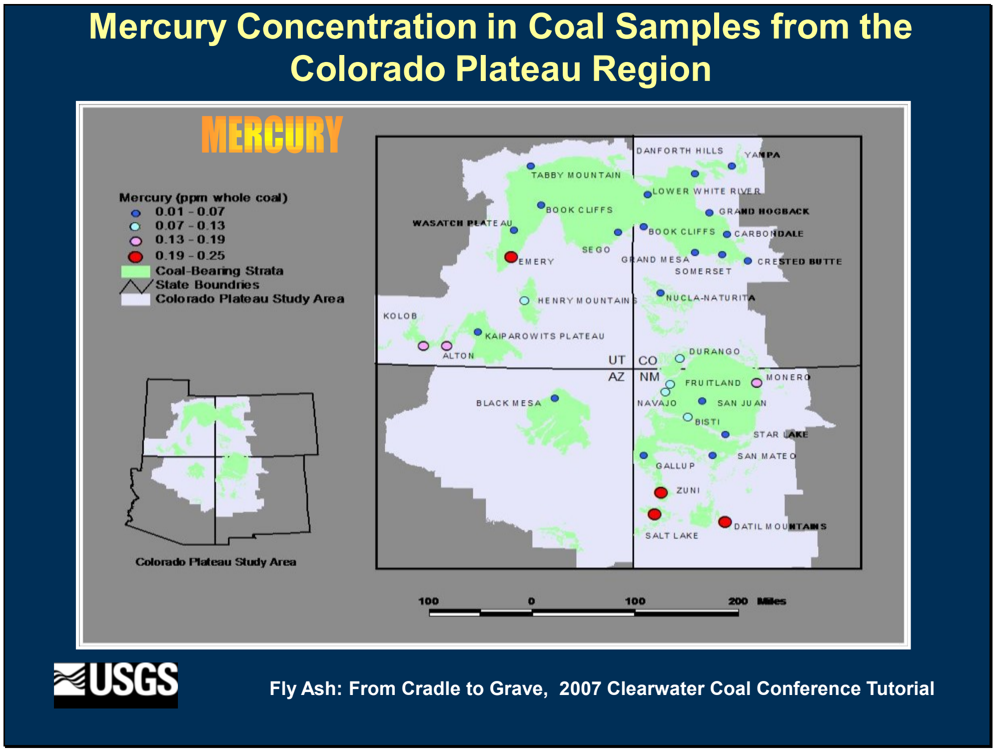
Slide 7



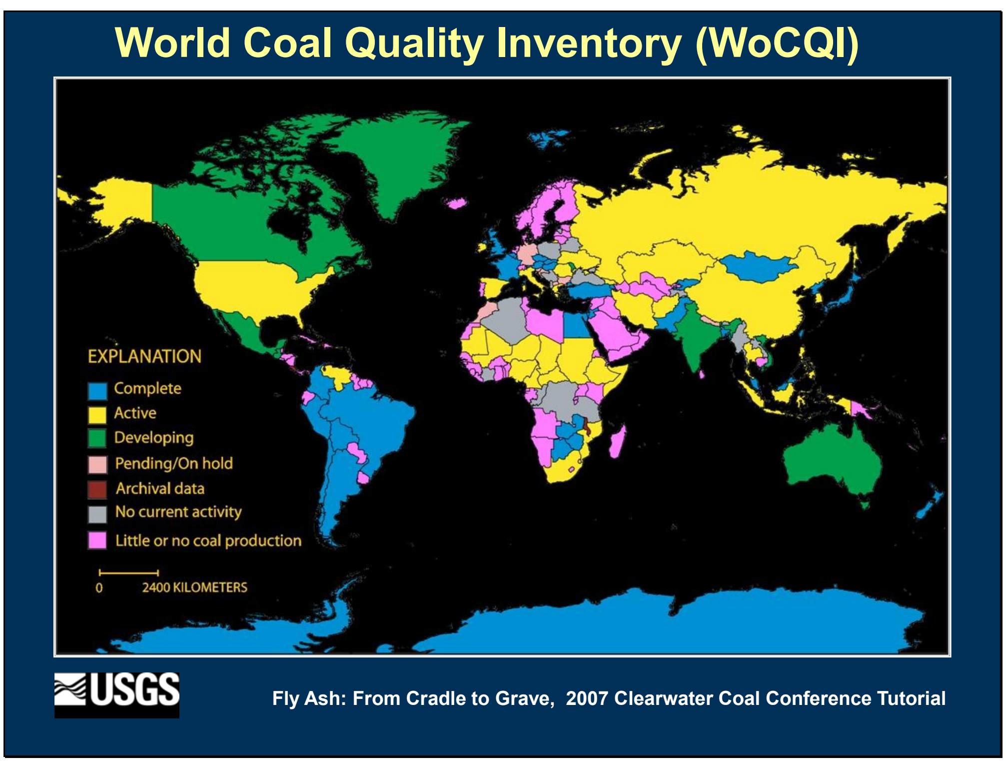
Slide 8



Slide 9



Slide 10



Slide 11

The Mission of the Energy Resources Program (ERP)

The ERP promotes and supports research resulting in original, geologically based,

non-biased energy information products

for policy and decision makers, land and resource managers, other federal and state agencies, the domestic energy industry, foreign governments, non-governmental groups, academia, and other scientists.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 12

The U.S. Geological Survey Energy Resources Program (ERP) 5-Year Plan

- Understand the processes critical to the formation, accumulation, occurrence, and alteration of geology based energy resources.
- Conduct scientifically robust assessments of those resources.
- Study the impact of energy resource occurrence and (or) production and use on both environmental and human health.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 13

Coal

- Improve the understanding of the coal endowment of the United States.
- Maintain state-of-the-art data management and data distribution systems in order to organize, provide ease of use, archive, and deliver critical ERP information both internally and externally.
- Partner with other organizations, including donor organizations, to address domestic and international issues regarding energy resources.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 14

Proposed Direction

Given increasing attention on the impacts of coal utilization, coal-quality research must address a more comprehensive suite of coal quality-related issues beyond fundamental coal quality parameters (such as ash yield, sulfur content, and heating value) and develop the possibility for a predictive capability addressing the effect of variations in spatial occurrence and coal utilization processes.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 15

The ERP should focus research efforts to support investigations into the current issues pertaining to coal production and beneficiation, and the impact of the coal combustion process and coal combustion products (CCPs).

Also provide information and data on a variety of coal quality parameters including sulfur, nitrogen, major-, minor-, and trace-elements, and coal mineralogy.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 16

Coal Quality: Geologic Controls and Utilization Issues Task

- Compile quality chemical information on the coals currently being mined and utilized throughout the United States. Evaluation of the distribution of element contents with emphasis between the feed coal and various coal combustion product (CCP) components.
- Relating that information to the geologic framework and possible environmental problems.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 17

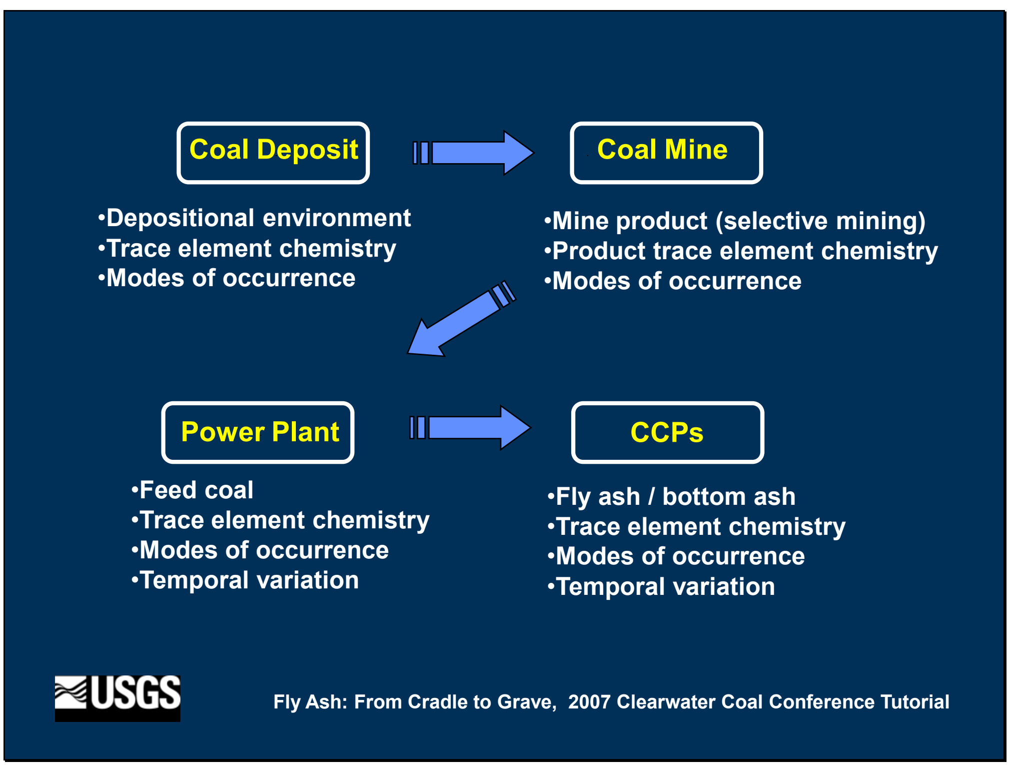
Coal Quality: Geologic Controls and Utilization Issues Task--Continued

- Studies should focus on how or where different quality parameters form and (or) occur, what happens to them through mining, production, transport, and, most importantly, utilization.
- Batch, flow through column, and sequential leaching studies to evaluate either disposal scenarios or to selectively dissolve mineral matter and help support microprobe, scanning electron microscope (SEM), and X-ray diffraction (XRD) analysis of selected inorganic elements.

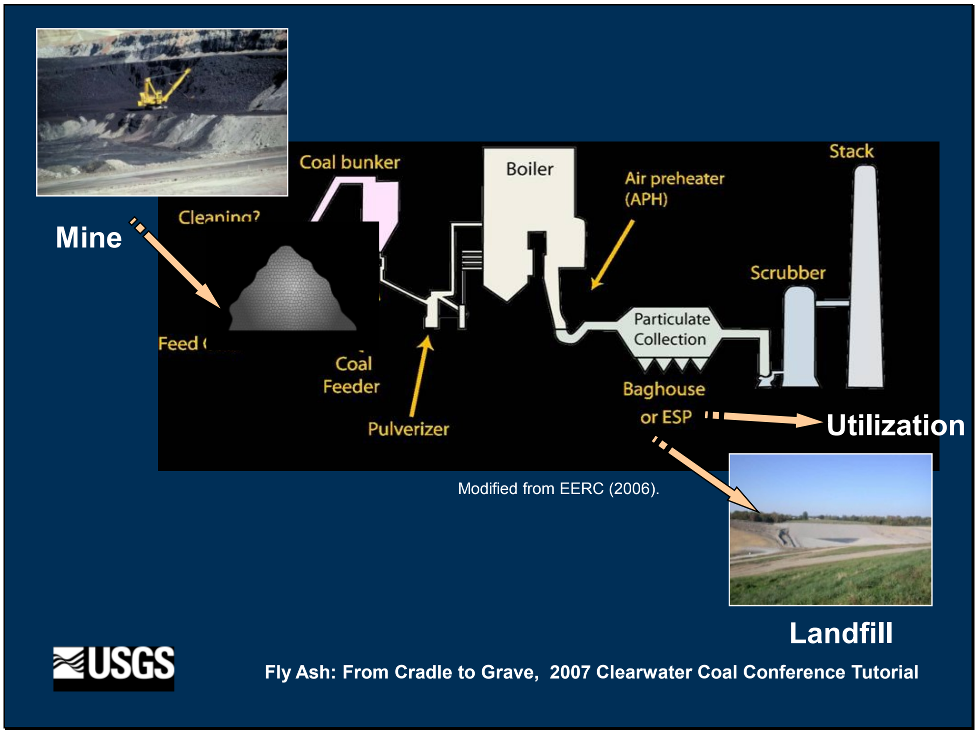
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

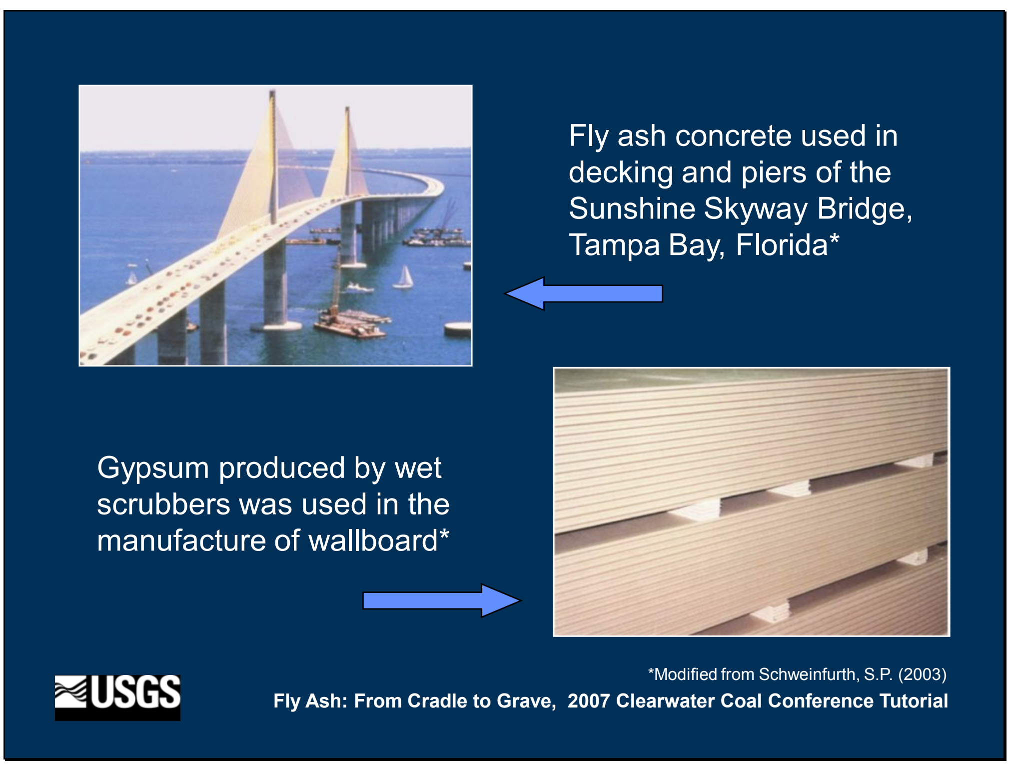
Slide 18



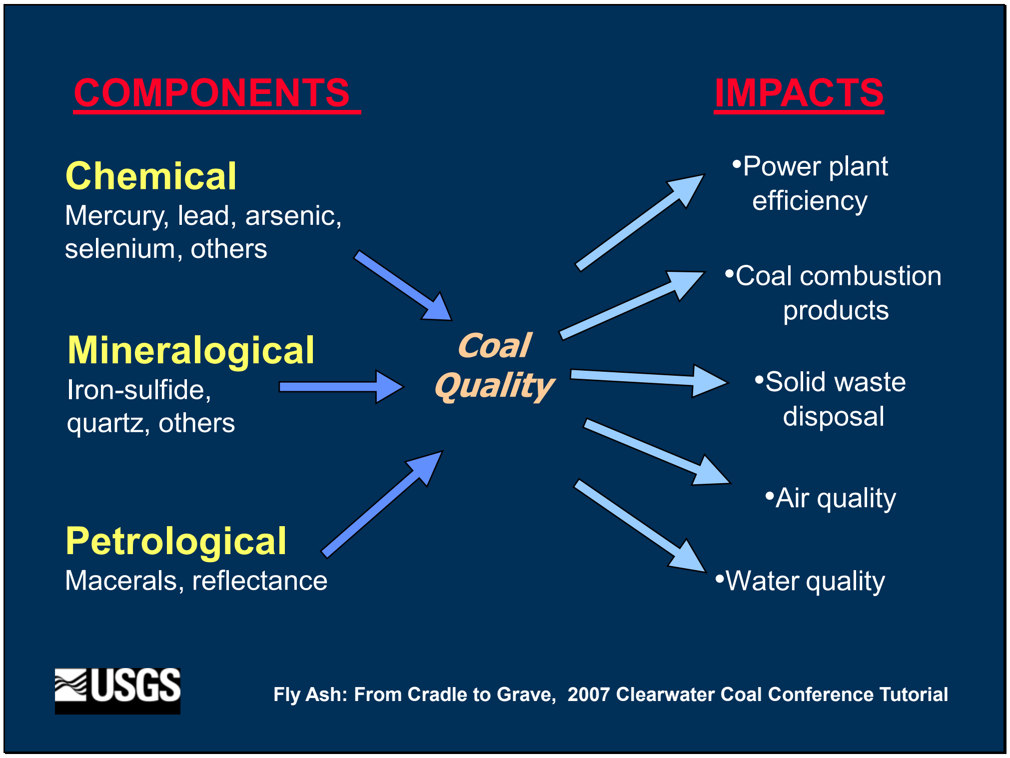
Slide 19



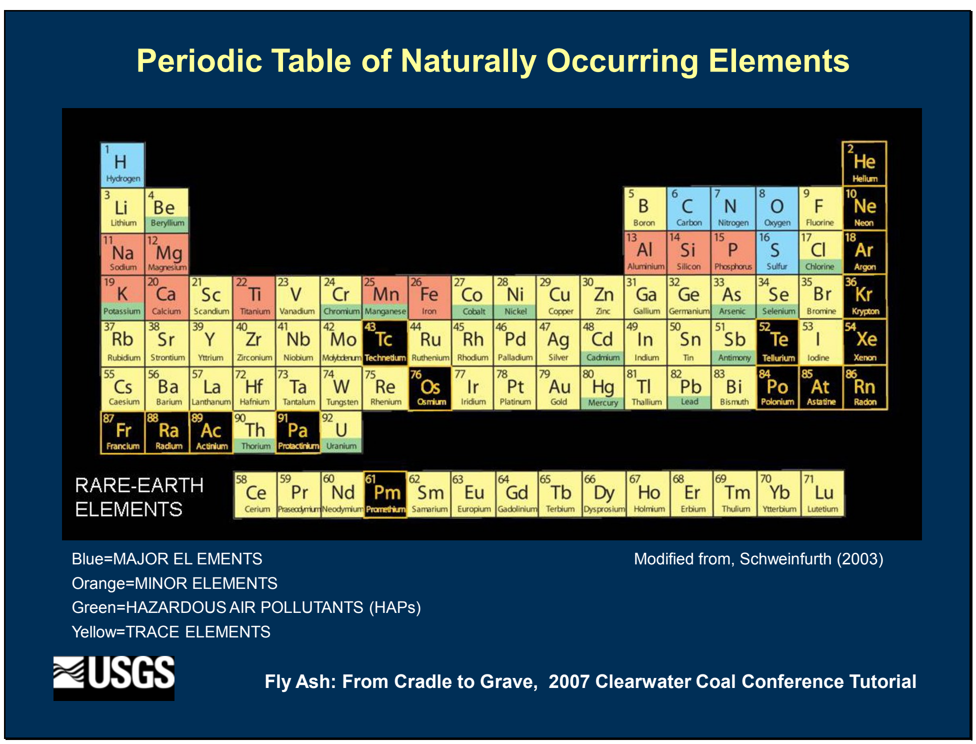
Slide 20



Slide 21



Slide 22



Slide 23

Elements of Environmental Interest

ELEMENT ppm whole coal	Tertiary coal Mean Value	Cretaceous coal Mean Value	Pennsylvanian Mean value
Antimony	0.63	0.48	1.1
Arsenic	7.4	1.6	11
Beryllium	1.1	1.2	2
Cadmium	0.1	0.1	0.43
Chromium	10	4.5	15
Cobalt	3.5	1.5	7
Lead	4.2	6.5	30
Manganese	60	22	70
Mercury	0.12	0.06	0.15
Nickel	4.6	3.7	20
Selenium	0.72	1.2	2.8
Uranium	1.7	1.3	1.8

ppm= parts per million

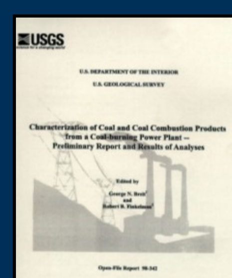
USGS

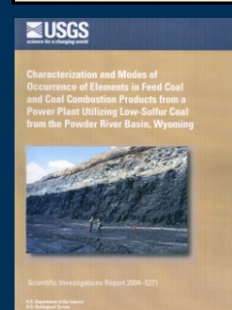
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 24

Previous Studies

- Kentucky- Multiple sources from Illinois and Appalachian Basins
- Indiana-Powder River Basin, Wyoming (7 mines-Wyodak/Anderson coal zone)
- Washington-Blend of Powder River Basin (Spring Creek) and Washington coal

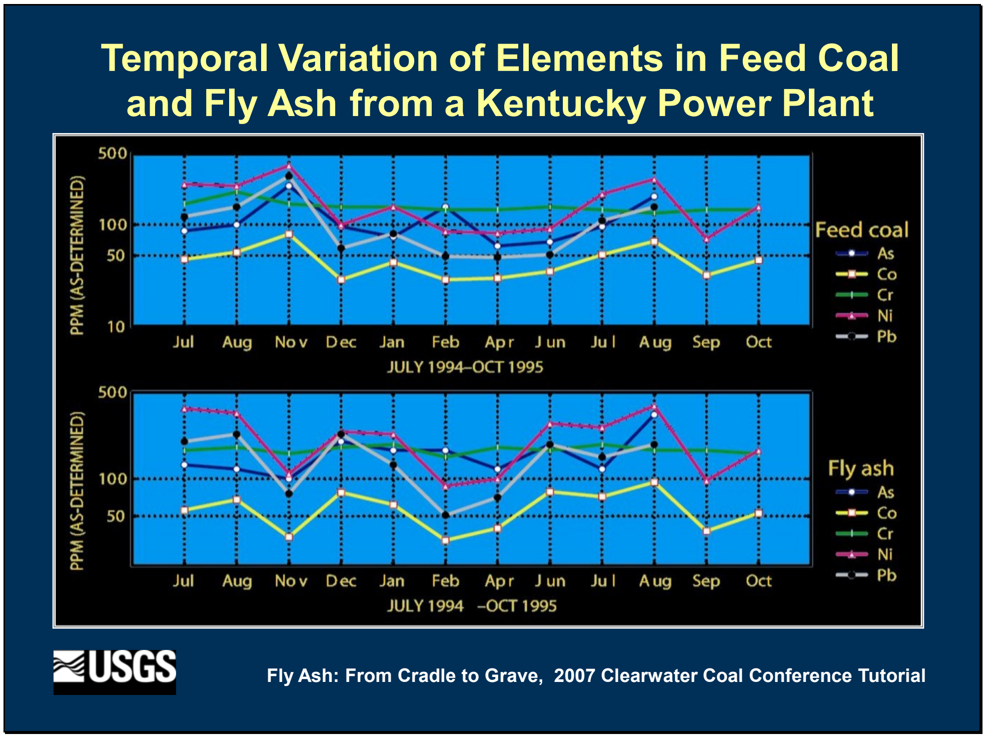




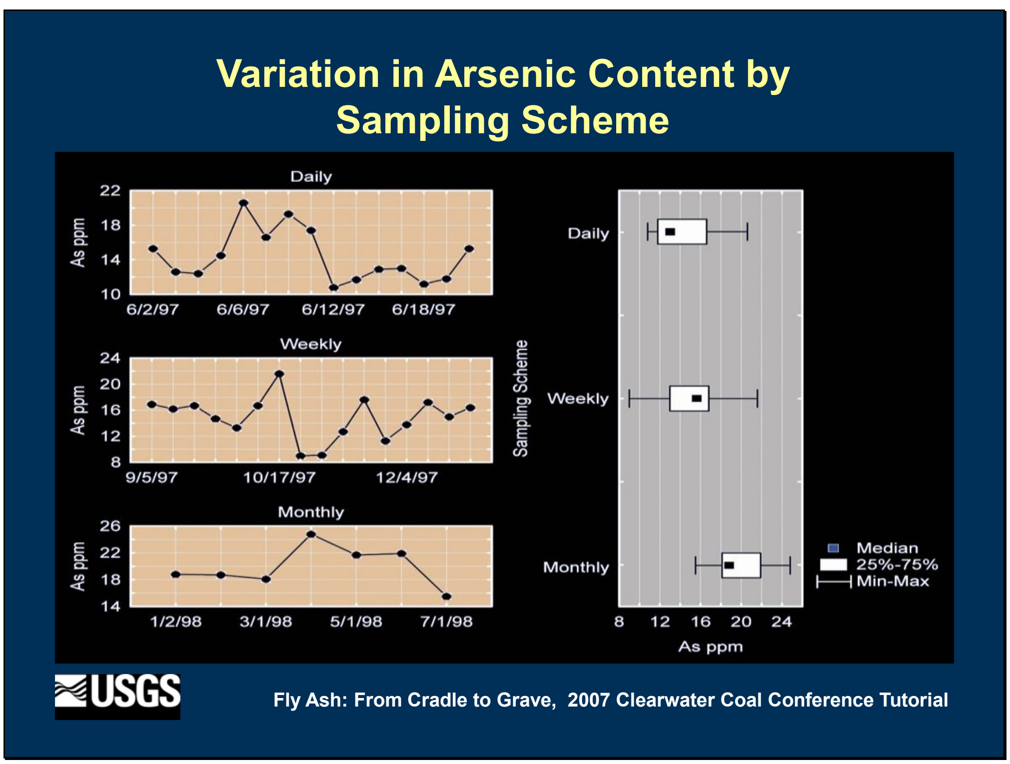
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

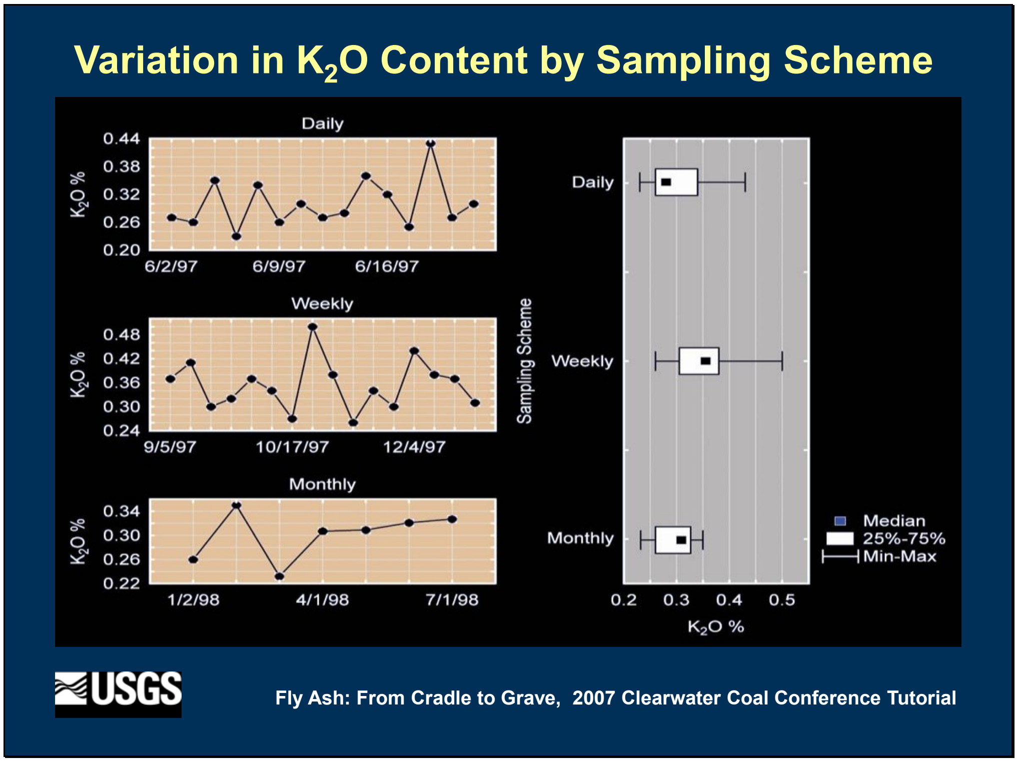
Slide 25



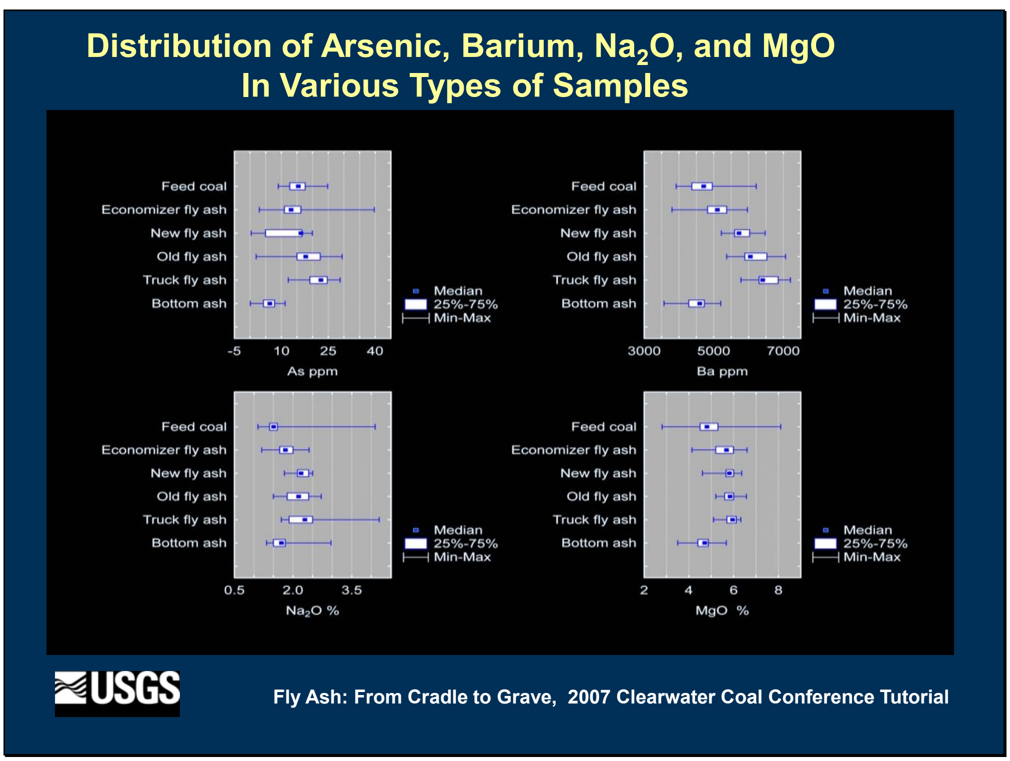
Slide 26



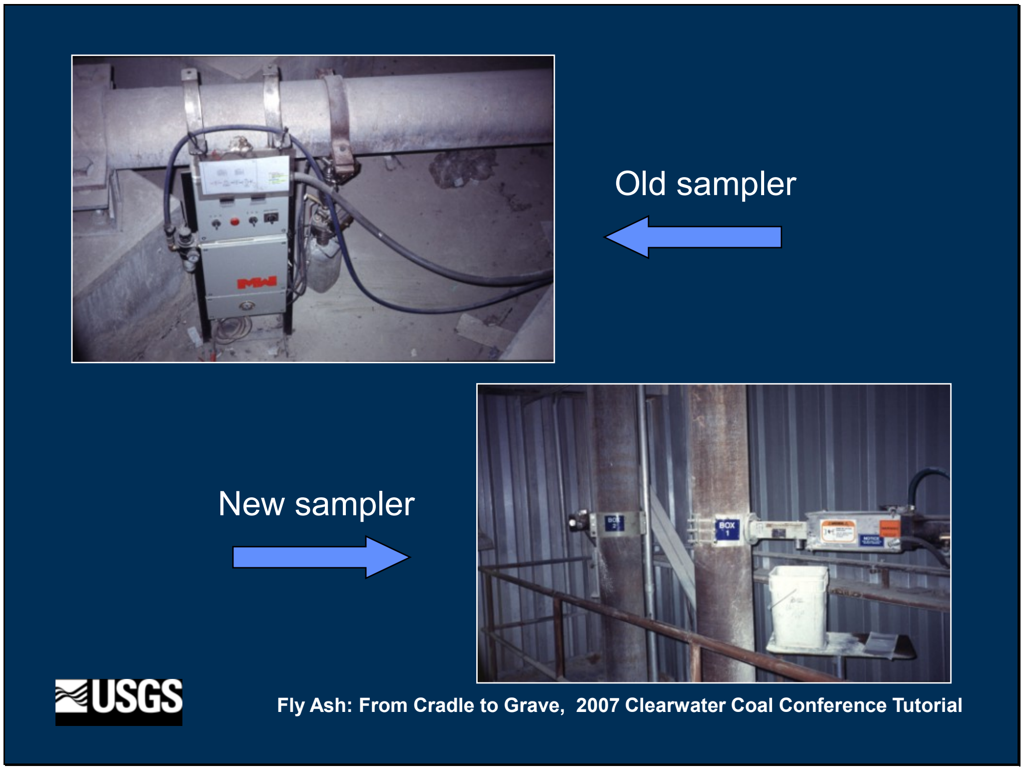
Slide 27



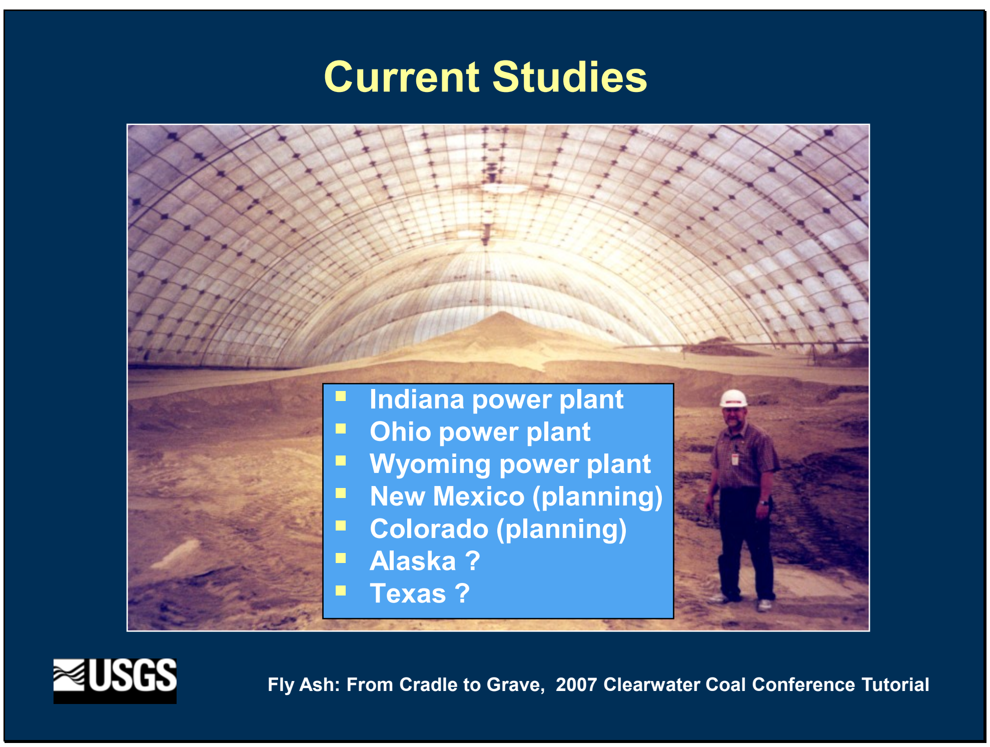
Slide 28



Slide 29



Slide 30



Slide 31

Benefits and Extensions of this Proposed Work

- There seems to be a lack of solid data, especially with regard to trace elements in the by-products. These studies could aid coal by-product utilization research.
- The creation of improved, practical databases to assist policy makers in making more informed decisions.
- Maintain high analytical standards (QA/QC) for the Energy Program Geochemistry Laboratory.
- Address coal ash disposal issues.

QA/QC=Quality Assurance/Quality Control

USGS **Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial**

Slide 32

Benefits to Contributors Data on Feed Coal and CCPs

- Trace element
- Proximate/ultimate, forms-of-sulfur, ash fusion temperatures, heat value
- Mineralogy (XRD, SEM, Microprobe)
- Petrography
- Leaching
- Interpretation of data
- Special samples

USGS **Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial**

Slide 33

There are Many Challenges, Especially Getting Cooperation from Mines and Utilities for Obtaining Representative Samples

- Private energy companies
- Environmental groups
- Consultants
- Educators, universities
- Utilities
- Other government agencies – DOE, EIA, NPS, BLM, NRC, EPA, SEC, OSM, State Geological Surveys (COOP)
- ASTM International
- American Coal Ash Association (ACAA)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Laboratory Setup, How Elements are Analyzed, and Quality Assurance/Quality Control (QA/QC)

Slide 34

USGS
science for a changing world

Laboratory Setup, How Elements are Analyzed, and Quality Assurance/Quality Control (QA/QC)

By
Jamey D. McCord
U.S. Geological Survey, Denver, Colorado

U.S. Department of the Interior
U.S. Geological Survey

Slide 35

Instructor

Jamey D. McCord

Jamey McCord is a physical scientist for the Central Region Energy Resource Team in Denver, Colorado. He has been with the U.S. Geological Survey for 12 years and is responsible for overseeing lab operations and maintaining the laboratory information system (LIMS). His primary focus is on coal, oil, and gas geochemistry.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 36

USGS Energy Program Geochemistry Laboratory Capabilities

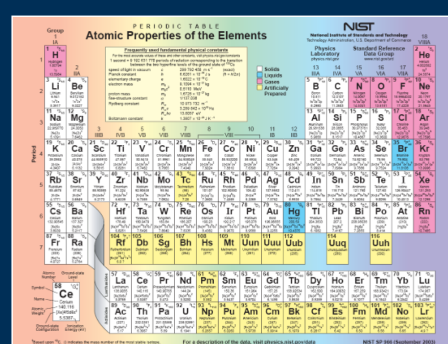
- Rock and coal
- Water
- Plant
- Gas and oil

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 37

Analysis Offered



Dragoset and others (2003)

- **ICP** (Inductively Coupled Plasma)
- **ICPMS** (Inductively Coupled Plasma Mass Spectrometer)
- **GFAA** (Graphite Furnace Atomic Absorption)
- Hydride / Cold vapor
- Sulfur by direct read
- Chloride by direct read
- Ash-Moisture-LOI (Lost on ignition)
- Custom analysis and method development

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 38

ICPAES (Inductively Coupled Plasma)

ICPAES is used to analyze major and trace elements in coal. It is capable of attaining values in the low parts per billion (ppb) range.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 39

ICPMS (Inductively Coupled Plasma Mass Spectrometer)

ICPMS is capable of analyzing coal to low parts per billion (ppb). It is also used for rare earths and limited isotopic ratioing.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 40

Sample Digestions for ICP and ICPMS

After the coal is received it is ashed and put through the appropriate digestion for the desired analyses.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 41

Different Digestions for ICP/ICPMS

Major Digestion

- Weigh 0.1 gram ash (LOI 750°C)

Trace Digestion

- Weigh 0.2 gram ash (LOI 500°C)

Sinter Decomposition

- Weigh 0.1 gram ash (LOI 500°C)

LOI= Lost on ignition

USGS

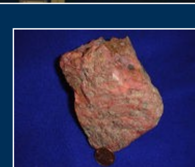
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 42

Mercury Analysis

HG analysis is done two ways:

- Direct read on the DMA (Direct Mercury Analyzer)
- Hydride generation on the FIMS (Flow Injection Mercury System)



Mercury Ore

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 43

Chloride Analysis

Tox-100 Direct Read Chloride Analyzer detects chloride down to 10 ppm compared to IC (Ion Chromatography) detection limits of 500-1,000 ppm.

ppm= Parts per million

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 44

Sulfur Analysis

LECO SC-432 for direct analysis of sulfur in coal. A coal industry standard for years.

Slide 45

Selenium Analysis

AA-200 used with a heating mantel and a flow injection system for selenium analysis. Detection limits are around 1ppm in coal.

ppm= Parts per million

Slide 46

Low Temperature Ashing

Low temperature ashing is done to preserve the crystal structure of minerals while removing organic matter that would interfere with X-ray diffraction analysis.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 47

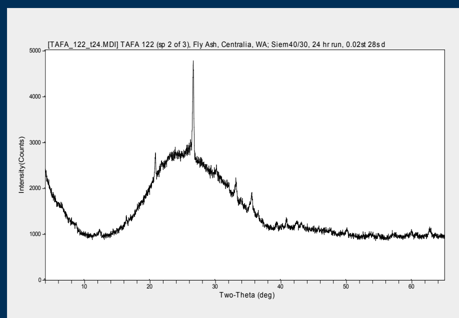
X-Ray Diffraction (XRD)

We have two X-ray diffraction units to provide mineralogical analysis. The Panalytical Expert-Pro is new and is making a big impact on how long it takes to analyze samples.

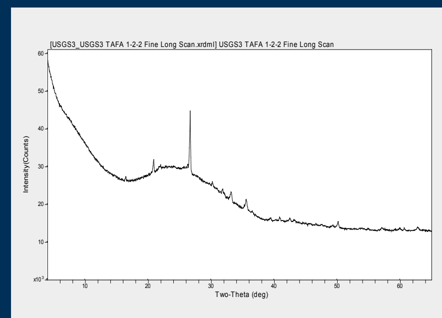
USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 48

Example of XRD Scan from New and Old



24 Hour Old



1 Hour New

The new XRD will bring speed and better mineral determinations.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 49

Geochemical Testing

Geochemical Testing is the contract laboratory used by the USGS Energy Resource Team to grind and split samples and to provide proximate and ultimate analysis.

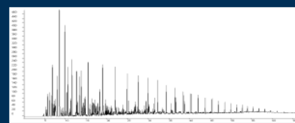
Geochemical Testing has been quality control tested by the USGS Energy Resource Team and has been a part of the lab audit.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 50

Organic Lab Capabilities



- API (Amer. Petroleum Inst.) gravity and weight percent sulfur
- Whole oil GC-FID (Gas Chromatography Flame Ionization Detector)
  - nC3 thru nC40
- Column chromatography
  - Saturate, aromatic, resin and asphaltene (SARA)
- GC-FID (Gas Chromatography Flame Ionization Detector)
  - Bitumen, saturate and aromatic fractions
- GC-MS (Gas Chromatography Mass Spectrometer) biomarker analysis
  - Whole oil
  - Bitumen, saturate and aromatic fraction
- Isotope ratio mass spectrometry (IRMS)
  - Whole oil bitumen, saturate and aromatic fraction
- Petrography and vitrinite reflectance
- Soxhlet extraction (bitumen)
- Elemental analysis

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 51

Quality Control in the Laboratory

The Energy Program Geochemistry Laboratory uses a three-tiered approach to quality control (QC).

- **The First Tier**
  Method Performance: QC samples are analyzed by laboratory personnel. At this level, laboratory personnel use the QC sample data to control the analytical process for each batch of samples. If the acceptance criteria are not met, the analysis is discontinued until corrected.
- **The Second Tier**
  Data Review and Blind Sample Programs: Laboratory personnel use data from these programs to monitor method performance throughout the laboratory and for long term tracking.
- **The Third Tier**
  Performance-Evaluation Studies: These studies are managed by private laboratories, local, State, and Federal agencies, all external to the Energy laboratory. Data from these studies can be used to compare laboratories or to select a laboratory for analytical work. Summary reports from many of these studies will be available on the Energy Program Geochemistry Laboratory web page.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 52

First Tier: Method Performance

- Energy laboratory personnel trying to determine elements in any sample evaluate two areas of performance: (1) instrument and (2) method. Accurate instrument operation can be verified by analyzing known standards at different concentrations. Blank water, which has negligible concentrations of the constituents of interest, is also analyzed to evaluate and eliminate potential sources of bias.

- The analyst uses QC samples to assess whether the method is working properly. Data produced from these samples are the most useful for customers to evaluate the labs entire analytical process. In addition to blank samples, standard reference materials are the primary tools for evaluating method bias and variability. Laboratory replicate data are also used to evaluate and obtain method variability information.

- Standard Reference Materials (SRMs) are obtained through internal and external sources, such as NIST, CANSPEX, USGS, and EPA. The SRM is thought to be sufficiently tested to be used to assess method performance. Several SRMs of differing concentrations and elements are analyzed alongside everyday samples. The SRM data are evaluated to assess bias for each analysis. Additionally, as the data are compiled, long-term estimates of method variability can be obtained.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 53

Second Tier: Data Review and Blind Sample Program

Data Review Program. All Energy laboratory analytical results initially are stored in the Laboratory Information Management System (LIMS) data base. A QC check is done by the laboratory manager to review all analytical results in the data base. Examples of QA checks include the following:

- Duplicate within limits
- SRMs fall within limits
- Internal blinds tests
- Internal standards
- Historical trends checked if available
- Correlation is within limits
- Proper amount of QA used in job

Blind Sample Programs. The blind sample programs are administered by internal and external personnel to the Energy laboratory. The internal program quantifies bias caused by random laboratory contamination. The external blind checks method performance and reproducibility.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 54

Third Tier: Performance-Evaluation Studies

The Energy laboratory participates in the following national and international inter-laboratory performance-evaluation studies: USGS Branch of Quality Systems Evaluation Program for Standard Reference Samples; CANSPEX

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 55

Outside Audit and Blind Program

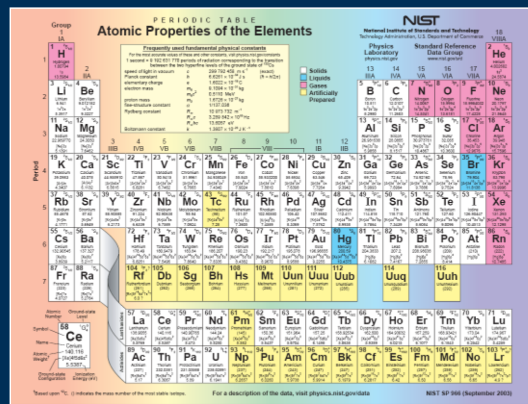
- The laboratory has gone through an outside audit to ensure its operations are consistent with the requirements of good laboratory practices specified in ISO 17025, ASTM D4621-99, and D4182-97.
- The laboratory also participates in a blind sample program and various round-robin sample programs to assure analytical quality.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 56

Energy Program Geochemistry Laboratory

- Geology
- Mineralogy
- Chemistry



Dragoset and others (2003)

All used to help with questions and arising problems in the coal, oil, and gas environment.

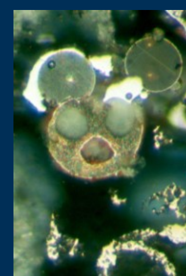
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Petrology of Feed Coal and Fly Ash

Slide 57

USGS
science for a changing world

Petrology of Feed Coal and Fly Ash

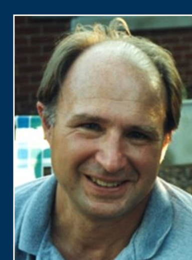


By
James C. Hower
University of Kentucky, Lexington

U.S. Department of the Interior
U.S. Geological Survey

Slide 58

Instructor



James C. Hower

Jim Hower is an adjunct professor at the University of Kentucky with his primary work conducted in the Environmental & Coal Technologies Group at the Center for Applied Energy Research. With the cooperation of the Kentucky Geological Survey and the U.S. Geological Survey, he maintains research in the petrology and geochemistry of coals. Much of the research is directed toward the utilization of coal and of products derived from coal. Recent research has focused on the mercury content of fly ash carbons.

Jim is the editor-in-chief of the *International Journal of Coal Geology*, was an author of the Atlas of Coal Geology (AAPG and The Society for Organic Petrology), and is the Eastern Region Director for the Combustion Byproducts Recycling Consortium (http://wvwri.nrcce.wvu.edu/CBRC/), a national program funded by the U.S. Department of Energy.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 59

Fly Ash Petrography

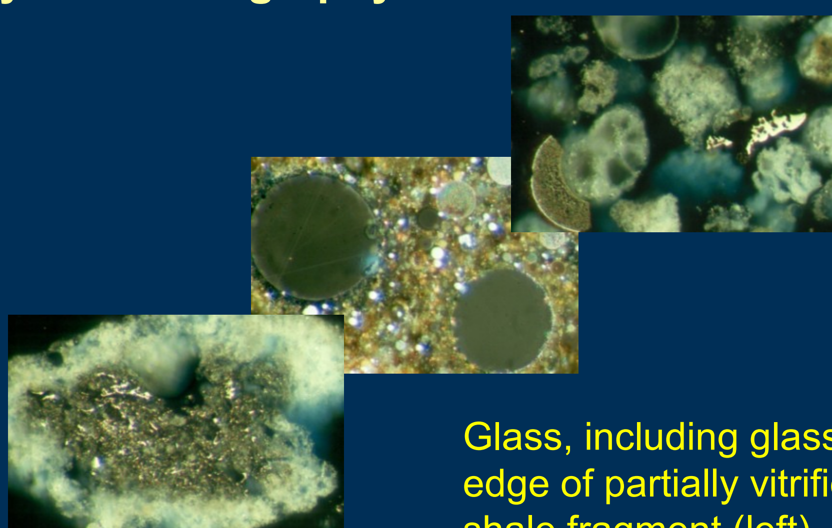
- Inorganic *neoformed*
  - glass
    - 70 to >90% of most FA
  - mullite
  - spinel
- Inorganic *coal derived*
  - Quartz

- Organic *neoformed*
  - isotropic coke
  - anisotropic coke
- Organic *coal (or fuel) derived*
  - inertinite
  - petroleum coke

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 60

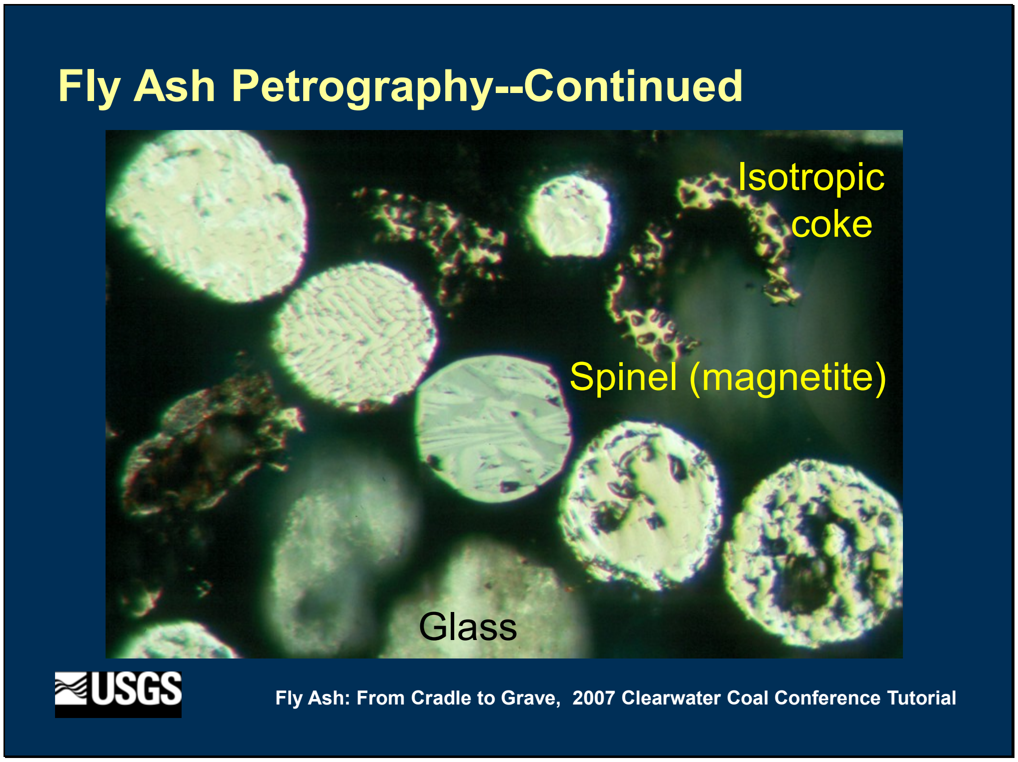
Fly Ash Petrography--Continued



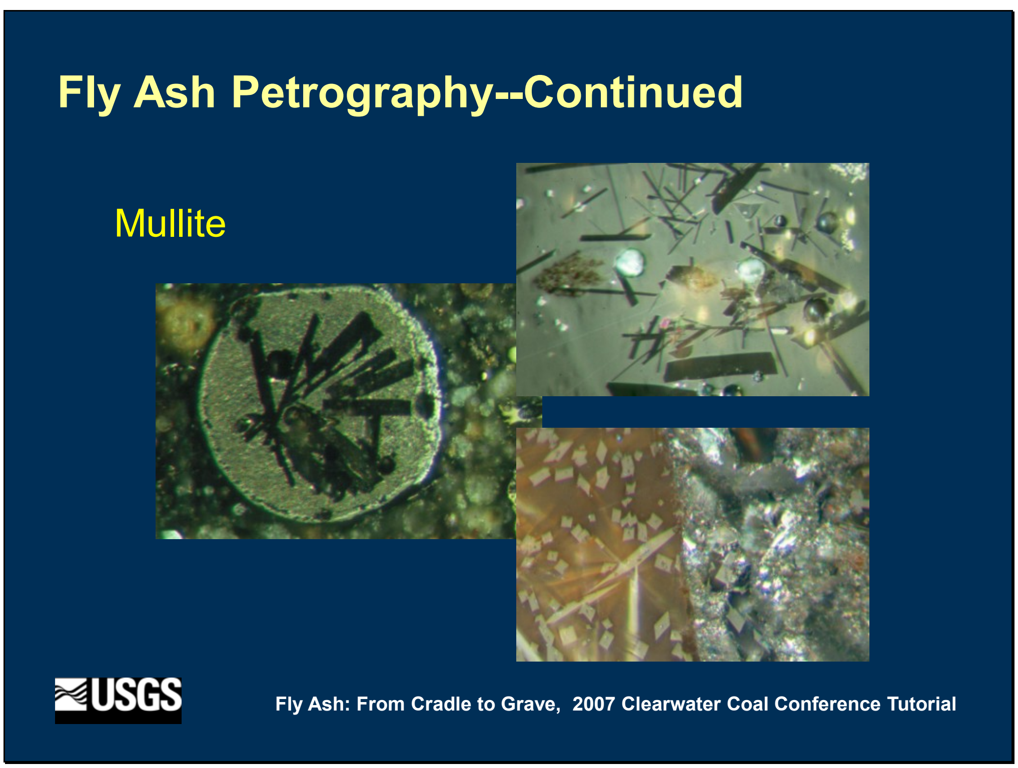
Glass, including glassy edge of partially vitrified shale fragment (left)

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

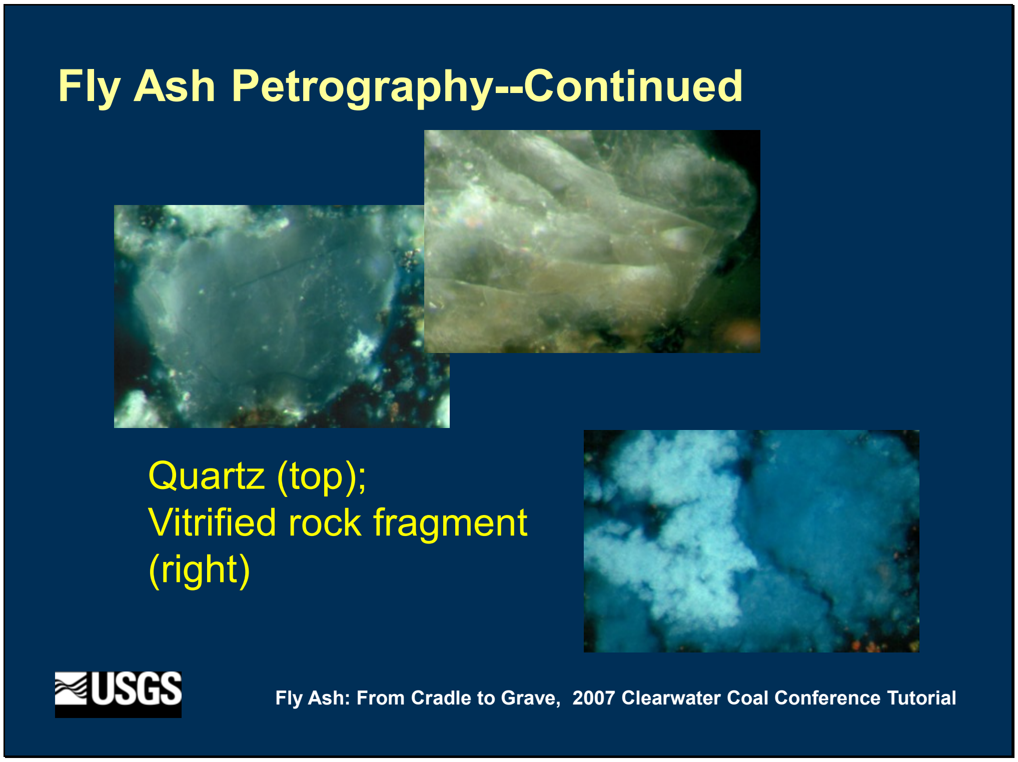
Slide 61



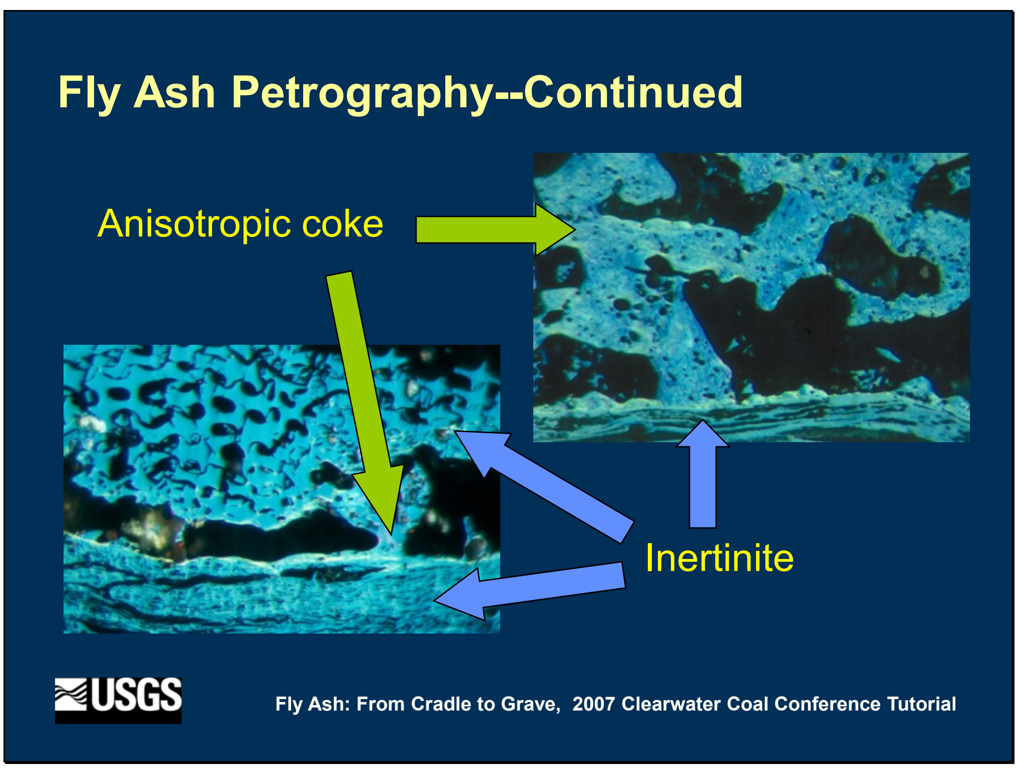
Slide 62



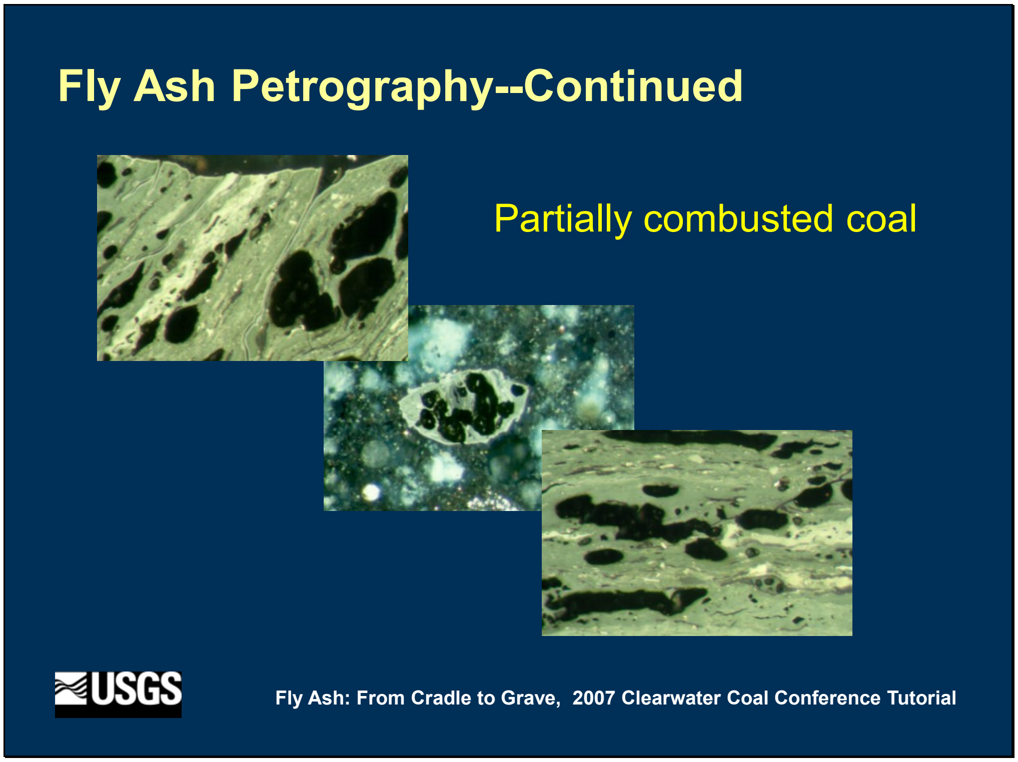
Slide 63



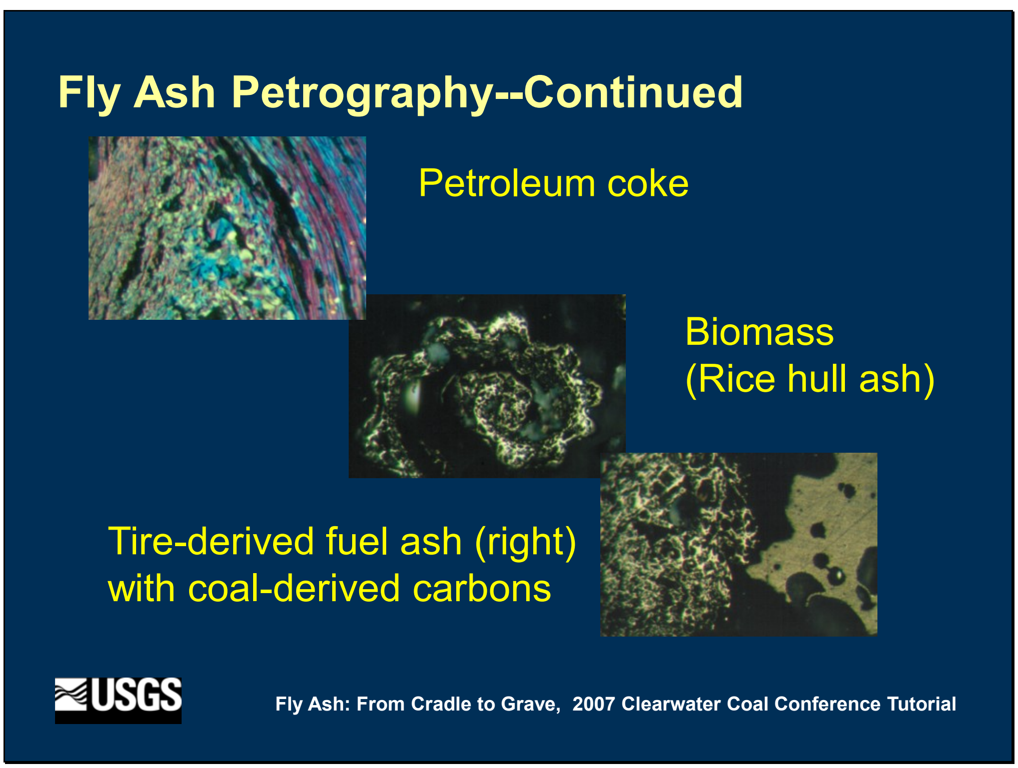
Slide 64



Slide 65



Slide 66



Slide 67

Fly Ash Chemistry

- Volatile trace elements display different characteristics in the ash-collection system
  - Arsenic, lead, zinc, and others will tend to be more highly concentrated in back rows of electrostatic precipitators (ESP)
  - Flue gas temperature decreases in direction away from boiler
  - Fly ash particle size decreases towards back rows
  - Therefore, cooler temperature (T) and greater surface area
- Most volatile elements, Hg is exception, tend to be associated with inorganic fly ash constituents

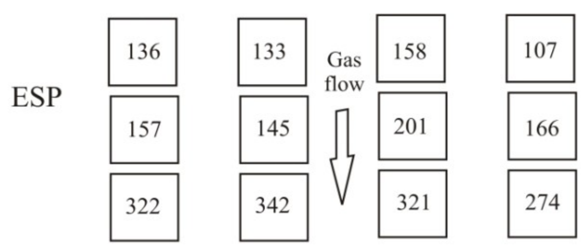
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 68

Fly Ash Chemistry--Continued

As Distribution (ppm)



Example from an eastern Kentucky power plant burning mid-S hvAb coal

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 69

Fly Ash Chemistry--Continued

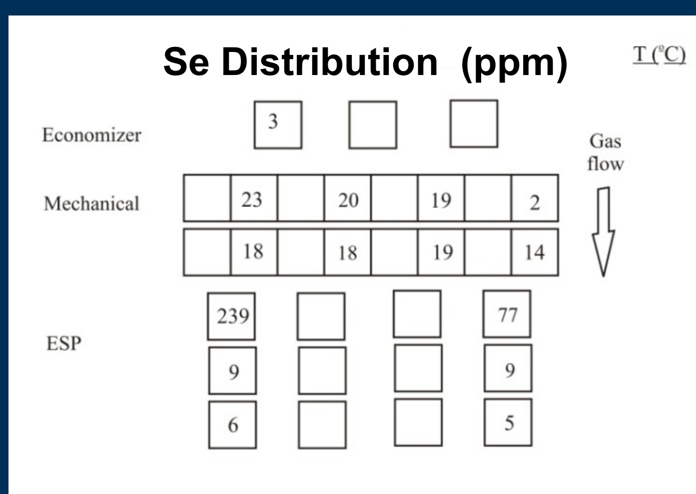
Selenium shows trends that are less distinct than latter elements

- Some power plants do show distinct increase towards cooler rows
- Others, as on next slide, show a distinct peak in warmer row
- More detailed study is underway

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 70

Fly Ash Chemistry--Continued



USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 71

Fly Ash Chemistry--Continued

Mercury capture by fly ash is complex, depends on:

- Speciation of Hg in flue gas
- T at collection point
- Amount of carbon in fly ash
- Type of carbon in fly ash

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 72

Fly Ash Chemistry--Continued

Factors influencing Hg speciation include:

- Coal rank influences on combustion temperature
- Amount of Cl in coal (greater in eastern US coals)
  - Enhances oxidation
- Amount of Ca in coal (greater in western US coals)
  - Inhibits oxidation
- Fe-oxides (greater in eastern coals) may catalyze oxidation of Hg

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 73

Fundamental Relations of Mercury with Fly Ash

Studies have demonstrated relations among:

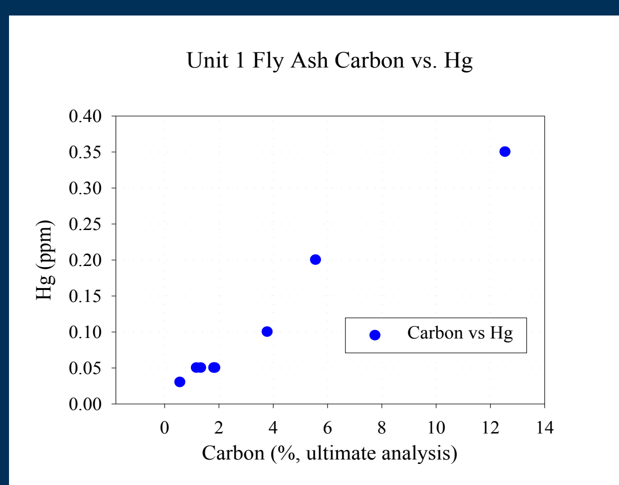
- **Amount of fly ash carbon and Hg capture**
  - More C = More Hg
- **Decreasing flue gas T and Hg capture**
  - Lower T = More Hg
- **Fly ash carbon type and Hg capture**
  - Increased Hg from inertinite to isotropic coke to anisotropic coke

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 74

Fundamental Relations of Mercury with Fly Ash--Continued



Hower and others (1999)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 75

Fundamental Relations of Mercury with Fly Ash--Continued

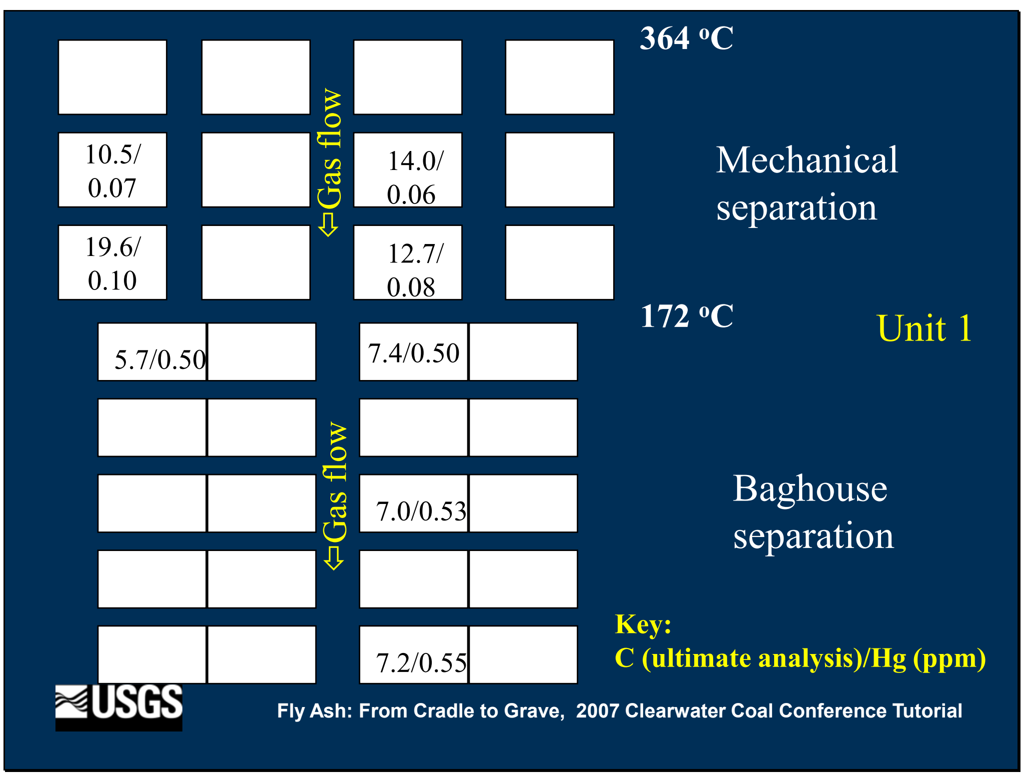
Studies have demonstrated relations among:

- **Amount of fly ash carbon and Hg capture**
  - More C = More Hg
- **Decreasing flue gas T and Hg capture**
  - Lower T = More Hg
- **Fly ash carbon type and Hg capture**
  - Increased Hg from inertinite to isotropic coke to anisotropic coke

USGS

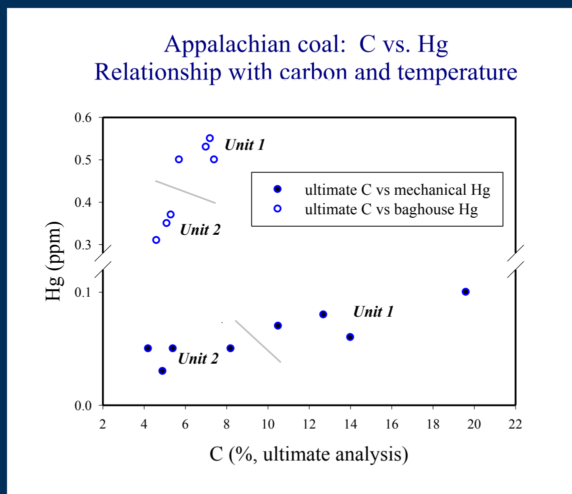
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 76



Slide 77

Fundamental Relations of Mercury with Fly Ash--Continued



Note greater concentration of Hg in cooler baghouse hoppers compared to concentration in mechanical hoppers, despite higher C in latter

Hower and others (2000)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 78

Fundamental Relations of Mercury with Fly Ash--Continued

Studies have demonstrated relations among:

- **Amount of fly ash carbon and Hg capture**
  - More C = More Hg
- **Decreasing flue gas T and Hg capture**
  - Lower T = More Hg
- **Fly ash carbon type and Hg capture**
  - Increased Hg from inertinite to isotropic coke to anisotropic coke
  - Surface area increases along same trend

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 79

Fundamental Relations of Mercury with Fly Ash--Continued

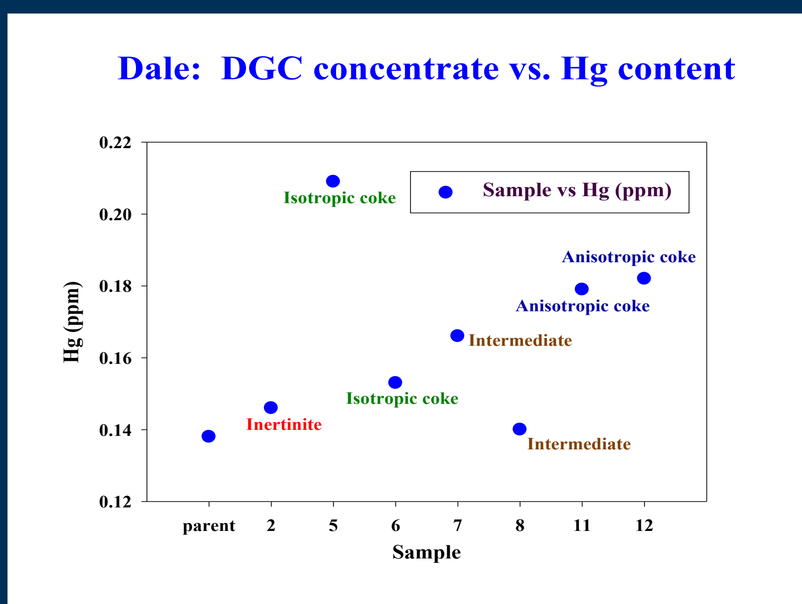
- Collected mechanical fly ash at 70 MW unit 3 at East Kentucky Power's Dale Station
- Screen ash at 140 mesh (106 microns)
- Concentrate C with triboelectrostatic separation
- Isolate C forms through density-gradient centrifugation (right)
- *Petrographic and chemical analyses of DGC splits*

Hower and others (2000)
Maroto-Valer and others (2001)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 80



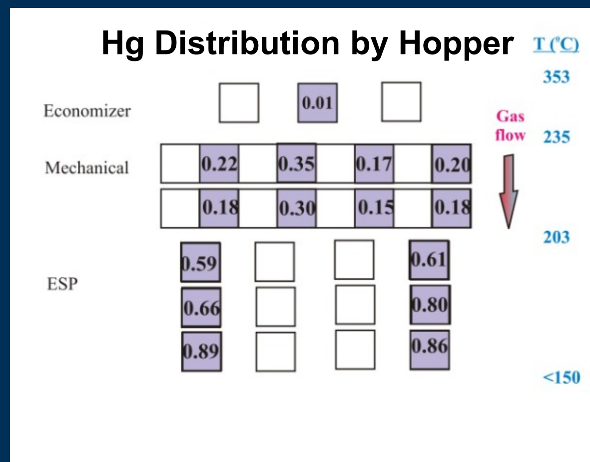
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 81

Fundamental Relations of Mercury with Fly Ash--Continued

Study of single-seam/ single-mine coal burned at 220-MW utility boiler (USGS NaCQI-funded study)



Mardon and Hower (2004)

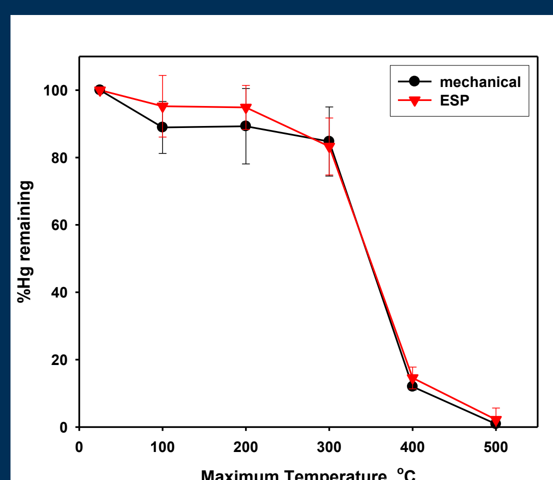
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 82

Fundamental Relations of Mercury with Fly Ash--Continued

Hg in fly ash has a reasonably good thermal stability, remaining in fly ash until 300-400°C range. Good indicator for stability in industrial utilization of fly ash.



Rubel and others (2006)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 83

Summary

- Fly ash has constituents that can be identified microscopically.
  - Combination of inherited and neoformed constituents from coal and, in some cases, from other fuels or contaminants
- Composition of fly ash is a function of chemistry of feed coal and other fuels, flue gas T at collection point, and fly ash petrology among other factors.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Characterization of Feed Coal and Fly Ash Using X-Ray Diffraction and Microbeam Methods

Slide 84

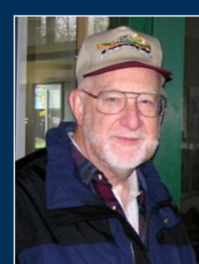
Characterization of Feed Coal and Fly Ash Using X-Ray Diffraction and Microbeam Methods

By
Michael E. Brownfield
U.S. Geological Survey, Denver, Colorado

U.S. Department of the Interior
U.S. Geological Survey

Slide 85

Instructor



Michael E. Brownfield

Michael Brownfield is a geologist with the U.S. Geological Survey in Denver, Colorado where he conducts studies on modes of occurrence of elements in coal and coal combustion products utilizing X-ray diffraction and microbeam techniques. Recent studies have focused on the characterization of feed coal and coal combustion products at an Indiana power plant burning Powder Basin coal and the characterization of coals and the modes of occurrence of elements (including Hg) from the Eocene Puget Group, John Henry No. 1 mine, King County, Washington.

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 86

Characterization of Feed Coal and Fly Ash

- Coal is a complex combustible rock made up of organic and inorganic mineral components.
- During combustion, elements present in the organic and mineral components of the coal are transformed into new gaseous and solid phases.
- In fly ash, elements may be uniformly distributed, enriched in certain grains or areas of grains, or present as coatings on grains or absorbed onto grain surfaces.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 87

Characterization of Feed Coal and Fly Ash--Continued

- Particle size, coal rank, amount of ash, coal mineralogy, and trace element content are important variables in controlling the combustion of coal and the mobility of elements in coal.
- For fly ash, the composition of the feed coal, combustion conditions, size of the fly ash particles, and fly ash mineralogy influence the distribution and mobility of trace elements.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 88

Mineralogy of Feed Coal and Fly Ash

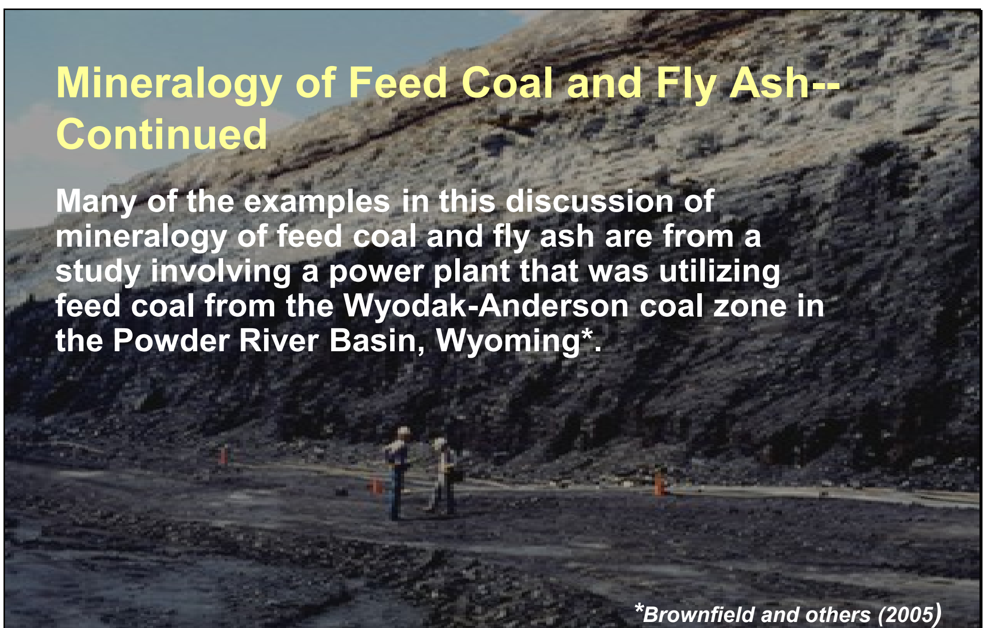
Determination of minerals in coal and fly ash is important because minerals can affect:

- Coal combustion and fly ash utilization and disposal
- Location (modes of occurrence) and leachability of elements in coal and fly ash
- Acidity (pH) during interaction with water

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 89



Mineralogy of Feed Coal and Fly Ash--Continued

Many of the examples in this discussion of mineralogy of feed coal and fly ash are from a study involving a power plant that was utilizing feed coal from the Wyodak-Anderson coal zone in the Powder River Basin, Wyoming*.

**Brownfield and others (2005)*

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 90

X-Ray Diffraction Analysis

Coal ash, for X-ray diffraction mineralogical studies, is derived by two methods:

- Low-temperature ashing (LTA) and
- Digesting the coal with aqueous sodium hypochlorite (NaOCl) or chlorine bleach

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 91

X-Ray Diffraction Analysis--Continued

X-ray diffraction methods:

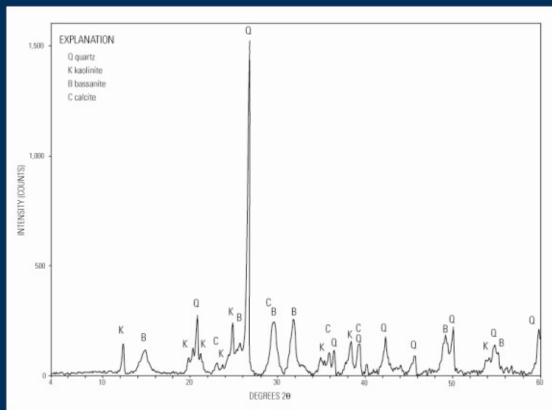
- X-ray diffraction data of bulk LTA and fly ash samples are digitally collected and analyzed. Relative abundance of minerals can be determined using reference intensity methods.
- Quantitative mineral data are determined on LTA ash and fly ash with Rietveld Refinement XRD methods (Larson and Von Dreele, 1994) using General Structure Analysis System (GSAS) and Materials Data Inc. (MDI) software. Rutile (TiO_2) can be added as a standard to determine amorphous material.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 92

X-Ray Diffraction Analysis--Continued

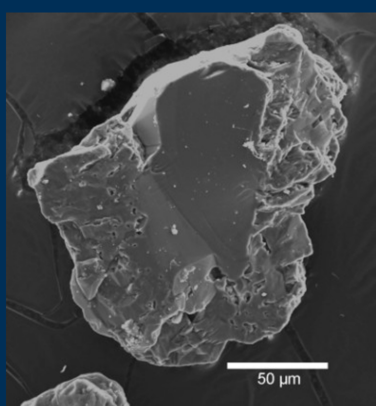


- X-ray diffractogram of low-temperature ash (LTA) from the Wyodak-Anderson, Powder River Basin, Wyoming
- Mean ash yield = 5.5 weight percent

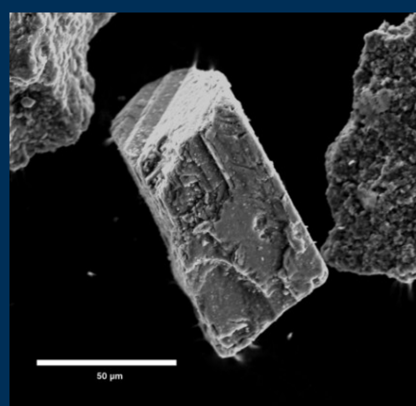
USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 93

X-Ray Diffraction Analysis--Continued



Quartz

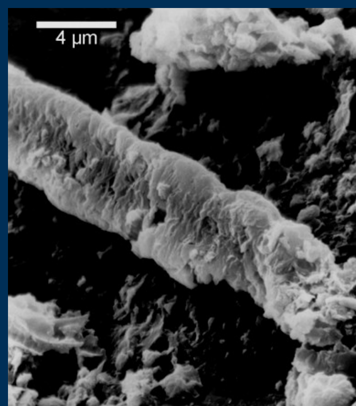


Subhedral crystal of calcite

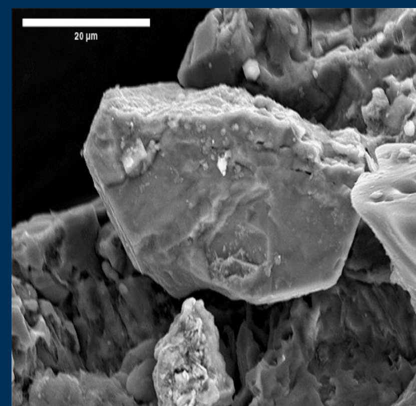
USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 94

X-Ray Diffraction Analysis--Continued



Kaolinite–$Al_2Si_2O_5(OH)$



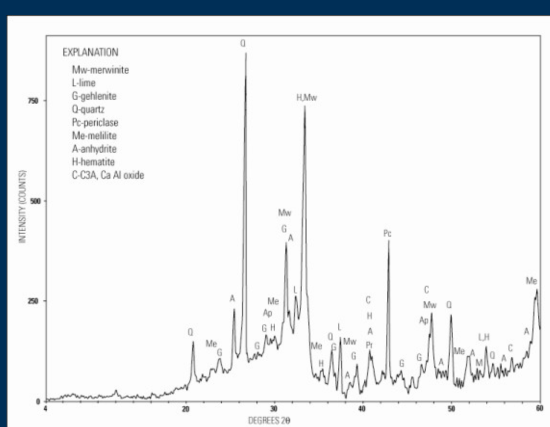
Subhedral crystal of gorceixite–$BaAl_3(PO_4)_2(OH)_5 \cdot H_2O$

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 95

X-Ray Diffraction Analysis--Continued



- X-ray diffractogram of fly ash derived from a Wyodak-Anderson feed coal, mined from the Powder River Basin, Wyoming
- Mean amorphous content = 60.4 percent, determined using General Structure Analysis System (GSAS) Rietveld software

USGS

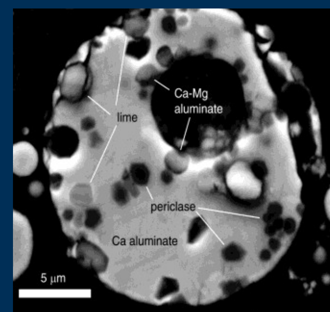
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 96

X-Ray Diffraction Analysis--Continued

Semiquantitative mineralogy of fly-ash samples from an Indiana power plant using feed coal from the Wyodak-Anderson coal zone, Powder River Basin, Wyo., determined by Rietveld X-ray diffraction analysis.
[nd, not detected]

Sample No. --- Mineral phase	RP1FAT	RP15FAT	RP22FAT	Average
Quartz SiO_2	8.7	6.8	6.7	7.4
Hematite -Fe_2O_3	2.6	1.5	2.0	2.0
Lime CaO	1.2	0.8	0.6	0.9
Anhydrite $CaSO_4$	3.2	4.3	3.8	3.8
Magnetite $Fe^{2+}Fe_2^{3+}O_4$	nd	0.9	0.5	0.7
Merwinite $Ca_3Mg(SiO_4)_2$	13.6	11.7	7.1	10.8
[1]C3A $Ca_3Al_2O_6$	4.0	4.1	4.2	4.1
Periclase MgO	3.1	2.6	1.8	2.5
Gehlenite $Ca_2Al(Al,Si)O_7$	7.4	10.2	7.8	8.5
Amorphous	56.1	59.2	66.0	60.4
Total	99.9	102.1	100.5	101.1



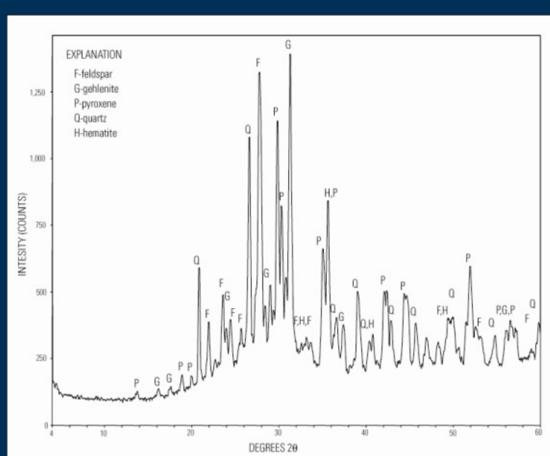
Fly ash grain derived from a feed coal mined from the Wyodak-Anderson coal zone, Powder River Basin, Wyoming.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 97

X-Ray Diffraction Analysis--Continued



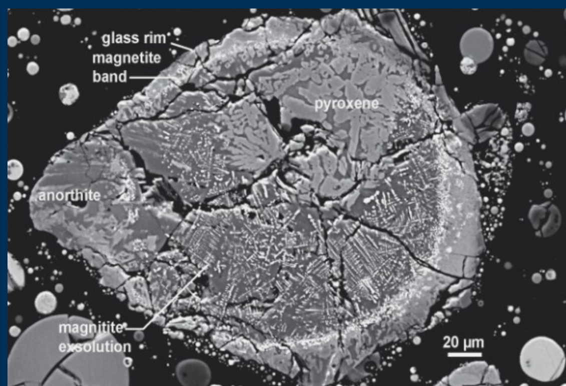
- X-ray diffractogram of bottom ash from the Wyodak-Anderson coal, Powder River Basin, Wyoming
- Bottom ash contains lesser amounts of amorphous material because of the increase in cooling time

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 98

X-Ray Diffraction Analysis--Continued



SEM image of a bottom ash grain from an Indiana power plant utilizing the Wyodak-Anderson coal from the Powder River Basin, Wyoming.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 99

Microbeam Analysis

Two electron microbeam instruments are utilized in the collection of coal and fly ash chemical and modes of occurrence data:

- Electron Probe Microanalyzer (EPMA), commonly known as a microprobe
- Scanning Electron Microscope (SEM)

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 100

Microbeam Analysis--Continued

Sample preparation:

- Polished epoxy-bound sections of coal and fly ash are prepared for the Electron Probe Microanalyzer and Scanning Electron Microscope.
- Low-temperature ash and sodium hypochlorite-treated samples are mounted on conductive carbon tape.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 101

Microbeam Analysis--Continued

The microprobe can collect both quantitative and semiquantitative chemical data:

- Quantitative chemical data (generally within ± 1 percent) on macrocrystalline phases greater than 5µm) using EPMA wavelength dispersive spectral (WDS) analysis is conducted using standards
- Semiquantitative analysis using energy dispersive X-ray analysis (EDS)

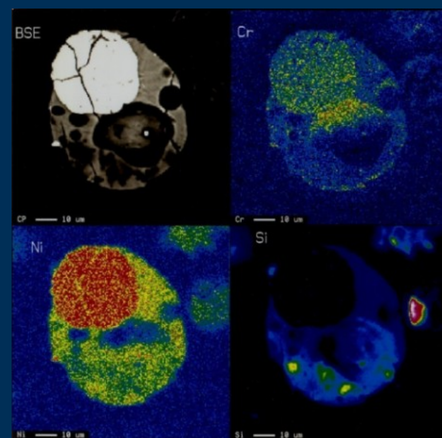
USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 102

Microbeam Analysis--Continued

X-ray intensity mapping with the microprobe:

- Very good in determining relative abundances and distribution of elements in a fly ash or bottom ash grain
- Can take as much as 8 hours to map a fly ash grain



Chromium, nickel, and silica in a ferrite-rich fly ash grain

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 103

Microbeam Analysis--Continued

Scanning Electron Microscope analysis (SEM):

- Imaging: using backscattered electron images (BEI) or secondary electron images (SEI)
- Semiquantitative analysis using Energy dispersive X-ray analysis (EDS)
- X-ray element intensity mapping, SEM scans are faster when compared to the microprobe

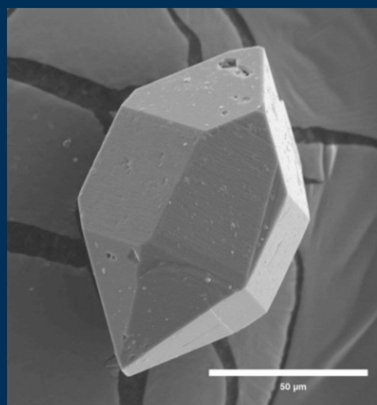
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

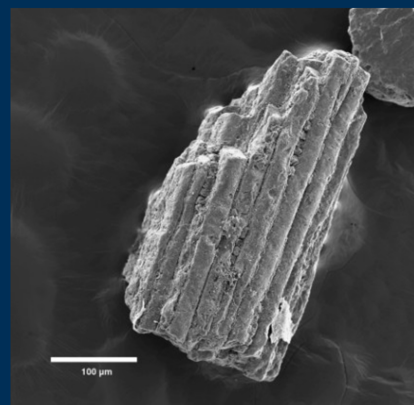
Slide 104

Microbeam Analysis--Continued

SEM Imaging



Euhedral beta-form quartz from digested coal.



Authigenic quartz that replaced plant matter, from digested coal.

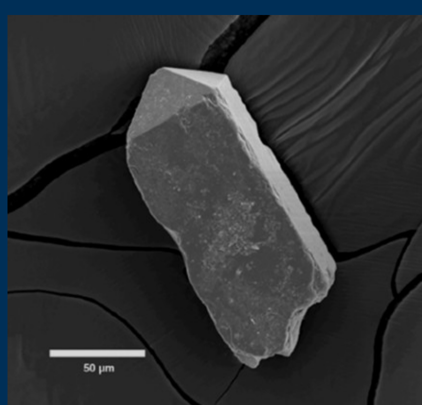
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

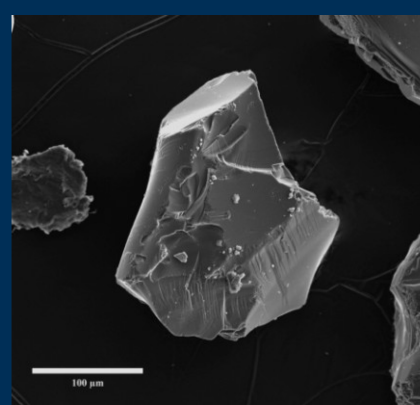
Slide 105

Microbeam Analysis--Continued

SEM Imaging



Euhedral crystal of zircon ($ZrSiO_4$) from digested coal.



Irregular cleavage fragment of K-feldspar from digested coal.

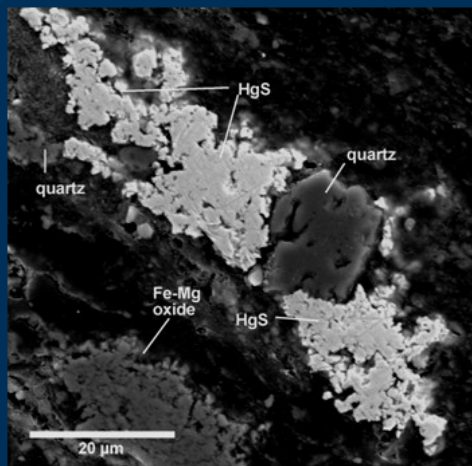
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 106

Microbeam Analysis--Continued

SEM Imaging



Secondary electron image (SEI) showing cinnabar (HgS), iron–magnesium oxide, and quartz in a polished sample of washed coal (specific gravity of 1.5 g/cm3) from the Franklin No. 12 coal bed in the John Henry No. 1 mine, King County, Washington.

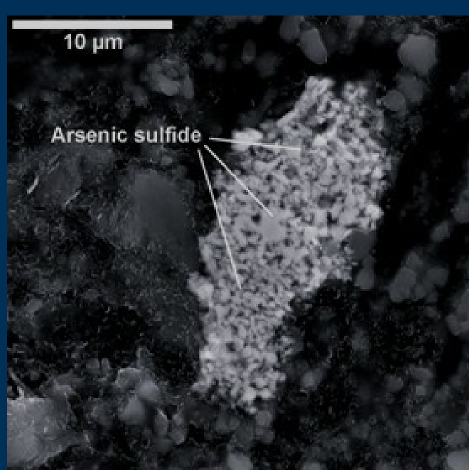
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 107

Microbeam Analysis--Continued

SEM Imaging



Secondary electron image (SEI) arsenic sulfide (realgar, AsS) from a washing plant reject sample from the Franklin 7–8 coal bed, John Henry No. 1 mine, King County, Washington.

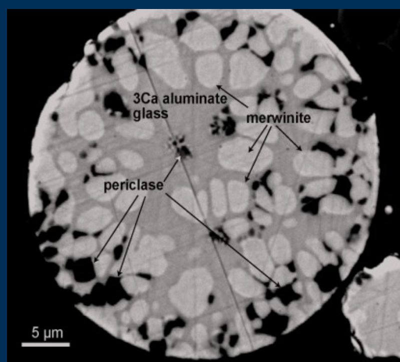
USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

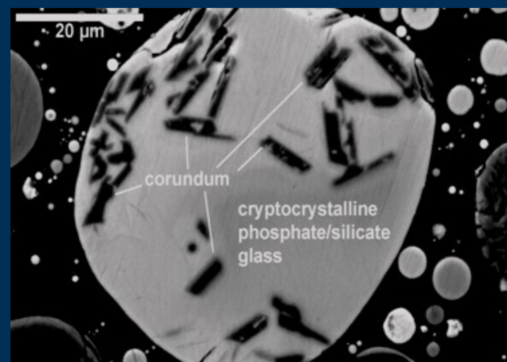
Slide 108

Microbeam Analysis--Continued

SEM Imaging



Ca+Mg- rich fly ash grain derived from a Wyodak-Anderson feed coal.



Phosphorus-rich fly ash grain derived from a Wyodak-Anderson feed coal.

USGS

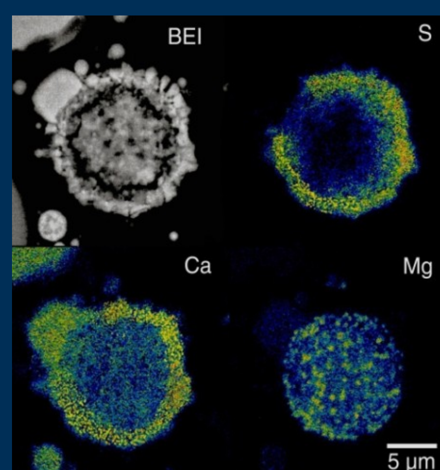
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 109

Microbeam Analysis--Continued

X-ray element intensity mapping:

SEM backscattered image (BEI) showing bright anhydrite ($CaSO_4$) and element X-ray intensity maps showing relative abundances and distribution of sulfur (S), calcium (Ca), and magnesium (Mg) from a fly ash grain derived from the a Wyodak-Anderson feed coal, Powder River Basin, Wyoming.



USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 110

Conclusions

X-ray diffraction and microbeam analysis of feed coal and CCPs are important tools in the characterization of feed coal and fly ash.

Determination of minerals and the chemistry of amorphous materials in coal and fly ash are important because these compounds can affect:

- Coal combustion and fly ash utilization and disposal;
- Location (modes of occurrence) and leachability of elements; and
- Acidity (pH) during interaction with water

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 111

Radiographic Analysis

Distribution of uranium in fly and bottom ash particles can be directly observed using fission-track radiography:

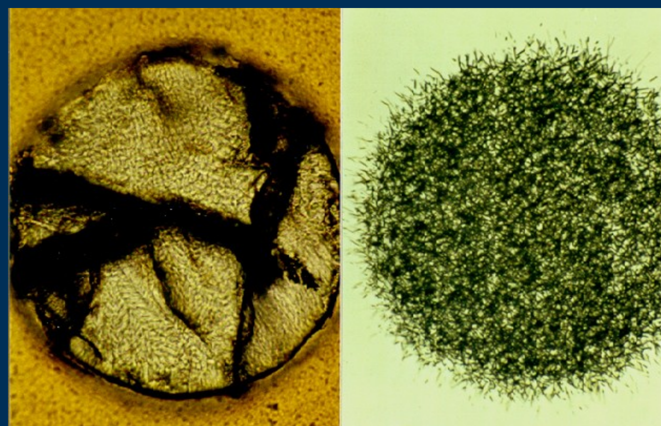
- Polished thin sections of grains of fly and bottom ash are prepared and irradiated with neutrons.
- During irradiation, fission fragments recoil from the surface of the thin section and pass into an overlying sheet of muscovite detector material causing linear paths of damage or tracks.
- High fission-track density can be related to areas of high uranium concentration in the sample.

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 112

Radiographic Analysis--Continued



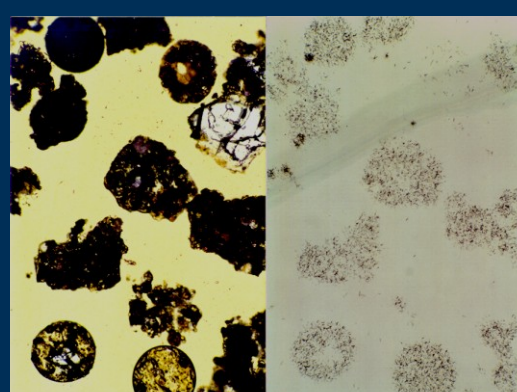
Photograph (left) of a Ca-P rich fly ash grain and its fission track radiograph. Size of images is about 0.25 by 0.15 mm.

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 113

Radiographic Analysis--Continued

Photography (left) of fly ash grains with mineral inclusions and its radiograph (right). Bright mineral inclusions are quartz and contain very low concentrations of uranium. Size of images are about 1.0 by 0.6 mm. Sample is fly ash derived from a Wyodak-Anderson feed coal, mined from the Powder River Basin, Wyoming.



USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Leaching Studies by Batch, Sequential, Toxicity Characteristic Leaching Protocol (TCLP), and Synthetic Precipitation Leaching Protocol (SPLP)

Slide 114

Leaching Studies by Batch, Sequential, Toxicity Characteristic Leaching Protocol (TCLP), and Synthetic Precipitation Leaching Protocol (SPLP)

By

Cynthia A. Rice

U.S. Geological Survey, Denver, Colorado

U.S. Department of the Interior
U.S. Geological Survey

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 115

Instructor

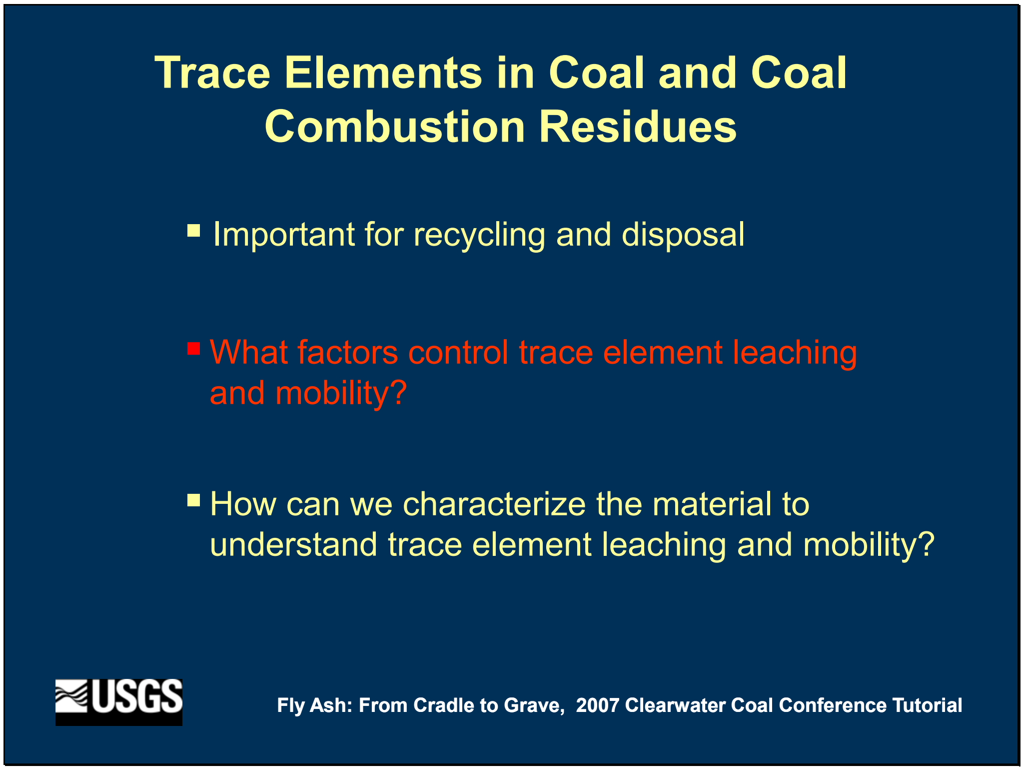
Cynthia A. Rice

Cyndi Rice is a retired U. S. Geological Survey scientist. She received a master's degree from the Colorado School of mines in geochemistry with an emphasis in aqueous geochemistry.

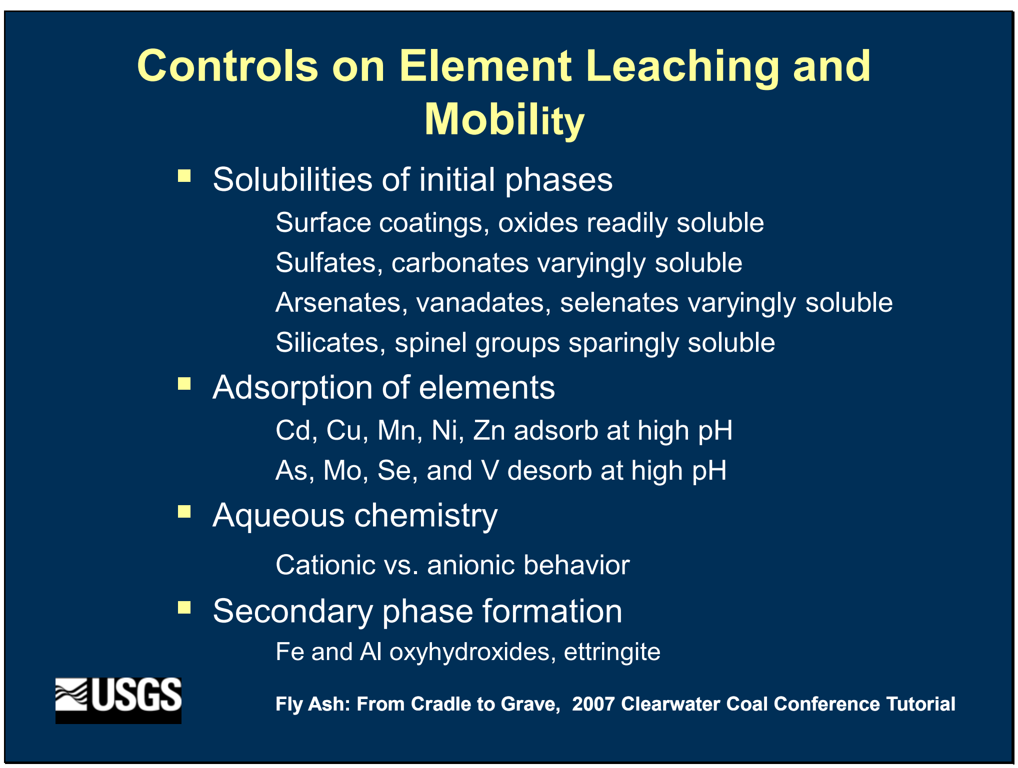
Cyndi has investigated the leaching behavior of trace elements in studies focusing on a power plant that utilized multi-source high and low S coals and a power plant that utilized a sole-source low S coal. More recently, Cyndi has devoted all of her time to environmental issues associated with the development of coalbed natural gas (CBNG). These studies include the characterization of waters co-produced with CBNG in the Ferron Sandstone in Utah and in the Fort Union Formation in the Powder River Basin. In addition, the interactions between CBNG water and the shallow subsurface are focuses of her studies.

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 116



Slide 117



Slide 118

Fast Reactions: Seconds to Minutes

Oxide Hydrolysis

$$CaO + H_2O \rightleftharpoons Ca^{2+} + 2OH^-$$

Coatings and Carbonates Dissolve

$$AlK(SO_4)_2 + H_2O \rightleftharpoons AlOH^{2+} + K^+ + 2SO_4^- + H^+$$

Secondary Phase Formation

$$FeOH^{2+} + OH^- \rightleftharpoons FeOOH + H^+$$

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 119

Intermediate to Slow Reactions: Days to Months

Glass Hydrolysis

$$NaAlSi_2O_6 + 2H_2O \rightleftharpoons Na^+ + Al^{3+} + 2SiO_2(aq) + 4OH^-$$

Secondary Phase Formation

$$2Al^{3+} + 3SO_4^{2-} + 6Ca^{2+} + 38H_2O \rightleftharpoons \text{Ettringite} + 12H+$$

CO_2 Equilibration

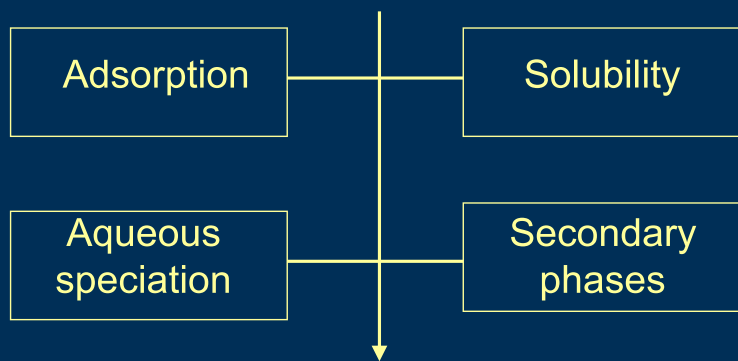
$$2CO_2 + Ca^{2+} + 2H_2O \rightleftharpoons CaCO_3 + HCO_3^- + 3H^+$$

USGS Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 120

“Master” Control on Leaching and Mobility

pH



Trace element leaching and mobility

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 121

Trace Elements in Coal and Coal Combustion Residues

- Important for recycling and disposal
- What factors control trace element leaching and mobility?
- How can we characterize the material to understand trace element leaching and mobility?

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 122

Variety of Leaching Tests

- Toxicity Characteristic Leaching Protocol (TCLP) EPA method 1311 using acetic acid with pH = 2.88 or 4.93 in 18 hour batch tests to simulate disposal in a municipal landfill
- Synthetic Precipitation Leaching Protocol (SPLP) Batch and column leaching using solution that mimics rainfall and disposal in environment exposed to precipitation
- Other: Deionized water, variety of reagents such as ammonium chloride, acetic acid, HCl, H_2SO_4, HNO_3, and HF

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 123

Strategy for Leaching Tests

- Determine environment of disposal or use:
  e.g. monofill, municipal landfill, mine fill, land application and exposure
- Select appropriate leaching protocol:
  e.g. TCLP, SPLP, batch, column, short time, longer time
- Apply leaching tests to determine representative behavior

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 124

Examples from Multi-source Power Plant

- High sulfur furnace

  2.5 – 3.5 weighted percent sulfur
  Feed coal, bottom ash, fly ash
  Precipitator temperature about 130°C

- Low sulfur furnace

  0.6 – 0.9 weighted percent sulfur
  Feed coal, bottom ash, 2 fly ashes
  Precipitator temperature about 470°C
  2 fly ashes are coarse and fine

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 125

Leaching Experiments

- 18 hour, 20:1 water to solid ratio
- < 1 hour, 20:1 water to solid ratio
- Column: > 64 flow days, water to solid ratio varied

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 126

18-Hour Batch Leach of Fly Ash

		pH	Cu	Zn	As	Mo	V
High S	Avg	11	<.0005	0.13	0.04	1.1	0.1
	% Total		<.004	0.10	0.47	48	0.65
Low S Coarse	Avg	8.3	0.13	0.013	0.06	0.30	0.15
	% Total		1.6	0.29	4.4	37	1.0
Low S Fine	Avg	4.6	4.2	0.55	0.02	0.099	0.025
	% Total		28	4.3	0.49	7.8	0.13

Averages for elements are in ppm

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 127

18-Hour Batch Leach of Fly Ash

		pH	Al	Ca	K	Na	SO_4
High S	Avg	11	9.4	310	11	15	450
	% Total		0.16	25	1.3	6.8	66
Low S Coarse	Avg	8.3	4.6	53	19	7.1	140
	% Total		0.06	13	1.8	4.8	77
Low S Fine	Avg	4.6	58	91	110	26	830
	% Total		0.73	18	11	14	100

Averages for elements are in ppm

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 128

18-Hour Batch Leach of Fly Ash

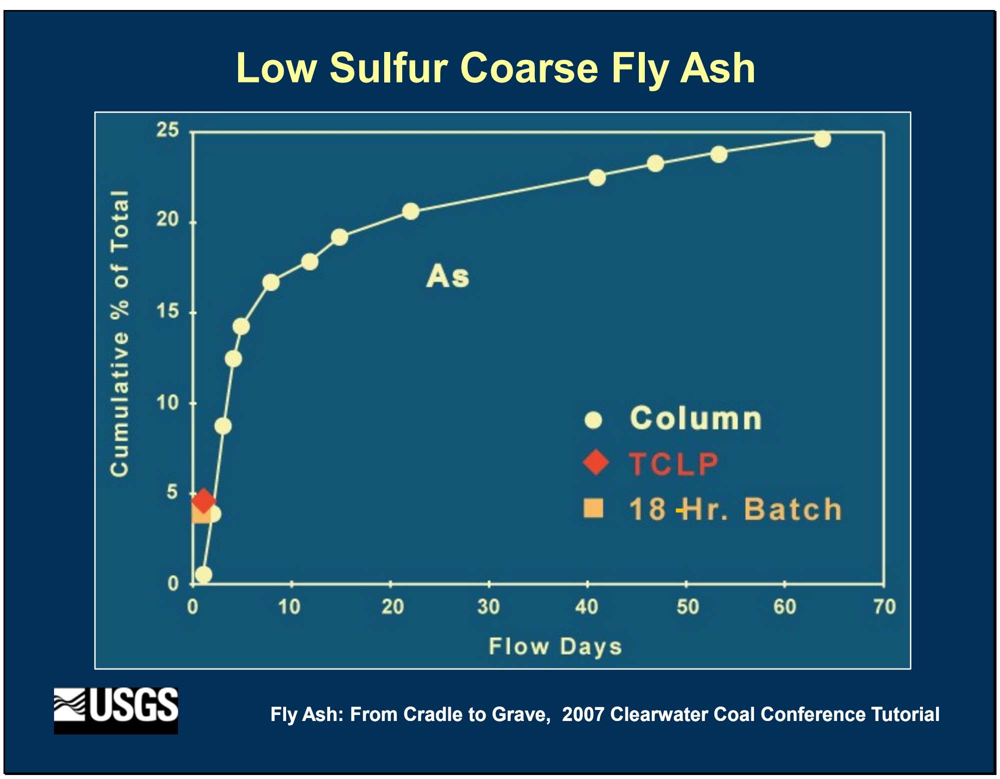
		pH	Al	Ca	K	Na	SO_4
High S	Min	9.1	0.24	230	1.3	8.4.	220
	Max	12	24	420	25	30	670
Low S Coarse	Min	4.7	0.08	21	9.0	2.9	74
	Max	10	10	100	35	22	220
Low S Fine	Min	3.3	0.007	53	15	6.5	150
	Max	8.1	170	140	220	10	1,900

Minimum and maximum values for elements are in ppm

USGS

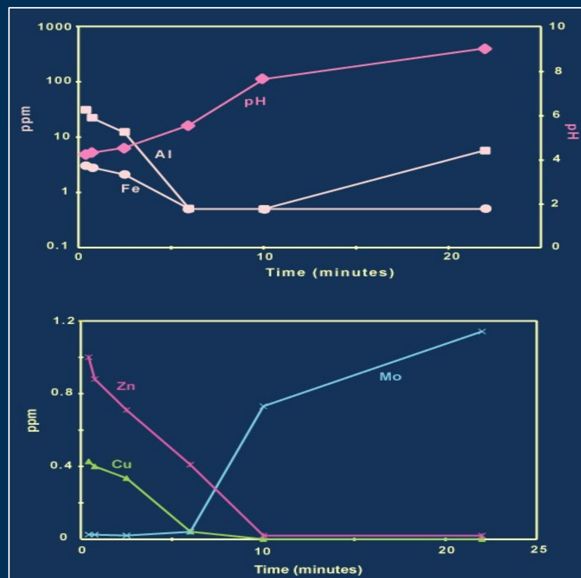
Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 129



Slide 130

High Sulfur Fly Ash--20:1 Water to Ash Ratio



USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

Slide 131

Summary

- Trace element leaching and mobility in coal and coal combustion residue depends primarily on pH
- Leaching tests can identify important reactions
- Multiple samples provide best estimate of behavior
- Recent research now provides basis for improved understanding of trace element behavior

USGS

Fly Ash: From Cradle to Grave, 2007 Clearwater Coal Conference Tutorial

References

Affolter, R.H., and Hatch, J.R., 1995, Cretaceous and Tertiary coals and coal-bearing rocks of the western United States; a bibliography of the U.S. Geological Survey data for resource estimation, quality determination, and reclamation potential evaluation: U.S. Geological Survey Circular 1108, p. 44-45.

Baedecker, P.A., Grossman, J.N., and Buttleman, K.P., 1998, National geochemical data base; PLUTO geochemical data base for the United States: U.S. Geological Survey DDS-47, CD-ROM.

Bragg, L.J., Oman, J.K., Tewalt, S.J., Oman, C.L., Rega, N.H., Washington, P.M., and Finkelman, R.B., 1998, Analytical data, sample locations, descriptive information, analytical methods and sampling techniques, database perspective, and bibliographic references for selected U.S. coal samples, *in* U.S. Geological Survey Coal Quality (COALQUAL) Database: version 2.0: U.S. Geological Survey Open-File Report 97-134, CD-ROM.

Brownfield, M.E., Affolter, R.H., Cathcart, J.D., Rice, C.A., Brownfield, I.K., O'Connor, J.T., Zielinski, R.A., Bullock, J.H., Jr., Hower, J.C., and Meeker, G.P., 2005, Characterization and modes of occurrence of elements in feed coal and coal combustion products from a power plant utilizing low sulfur Powder River basin coal: U.S. Geological Survey Scientific Investigations Report 2004-5271, 36 p.

Dragoset, R.A., Musgrove, A., Clark, C.W., and Martin, W.C., 2003, Periodic table atomic properties of the elements: Physics Laboratory, National Institute of Standards and Technology (NIST), Technology Administration, U.S. Department of Commerce, NIST SP 966, poster available at http://physics.nist.gov/PhysRefData/PerTable/index.html.

EERC (Energy and Environmental Research Center), 2006, Mercury in coal and transformations in combustion flue gases, *in* Mercury Control Short Course: EERC, September 7, 2006, Denver Airport Marriott at Gateway Park, Denver, Colorado, p. 18.

Ellis, M.S., 1995, Bibliography of publications by members of the Branch of Coal Geology, Office of Energy and Marine Geology, U.S. Geological Survey, January 1, 1985-September 30, 1994: U.S. Geological Survey Open-File Report 95-65, 194 p., http://pubs.usgs.gov/of/1995/ofr-95-0065-a/.

Finkelman, A.C., Wong, C.J., Cheng, A.C., Finkelman, R.B., 1991, Bibliography of publications containing major, minor, and trace element data from the National Coal Resources Data System: U.S. Geological Survey Open-File Report 91-123, 19 p.

Hower, J.C., Trimble, A.S., Eble, C.F., Palmer, C.A., and Kolker, Allan, 1999, Characterization of fly ash from low-sulfur and high-sulfur coal sources: partitioning of carbon and trace elements with particle size: Energy Sources, v. 21, p. 511-525.

Hower, J.C., Finkelman, R.B., Rathbone, R.F., and Goodman, J.H., 2000, Intra- and inter-unit variation in fly ash petrography and mercury adsorption: examples from a western Kentucky power station: Energy & Fuels, v. 14, p. 212-216.

Hower, J.C., Maroto-Valer, M.M., Taulbee, D.N., Sakulpitkakphon, Tanaporn, 2000, Mercury capture by distinct fly ash carbon forms: Energy & Fuels, v. 14, p. 224-226.

Larson, A.C., and Von Dreele, R.B., 1994, General Structure Analysis System (GSAS): Los Alamos National Laboratory Report 86-748, 231 p.

Mardon, S.M., and Hower, J.C., 2004, Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant: International Journal of Coal Geology, v. 59, p. 153-169.

Maroto-Valer, M.M., Taulbee, D.N., and Hower, J.C., 2001, Characterization of the carbon types present in fly ash separated by density gradient centrifugation: Fuel, v. 80, p. 795-800.

Rubel, A.M., Hower, J.C., Mardon, S.M., and Zimmerer, M.J., 2006, Thermal stability of mercury captured by ash: Fuel, v. 85, p. 2509.

Schweinfurth, S.P., 2003, Coal—a complex natural resource; an overview of factors affecting coal quality and use in the United States, with a contribution on coal quality and public health by Finkelman, R.B.: U.S. Geological Survey Circular 1143, 39 p.

Wood, G.H., Jr., Kehn, T.M., Carter, M.D., and Culbertson, W.C., 1983, Coal resource classification system of the U.S. Geological Survey: U.S. Geological Survey Circular 891, 65 p.

Contact Information

Ronald H. Affolter, Box 25046, MS 939, Denver Federal Center, Denver, Colorado 80225, 303-236-7752, affolter@usgs.gov

Michael E. Brownfield, Box 25046, MS 939, Denver Federal Center, Denver, Colorado 80225, 303-236-5742, mbrownfield@usgs.gov

Margaret S. Ellis, Box 25046, MS 939, Denver Federal Center, Denver, Colorado 80225, 303-236-7775, mellis@usgs.gov

James C. Hower, 2540 Research Park Dr., Lexington, Kentucky 40511, 859-257-0261, hower@caer.uky.edu

Jamey D. McCord, Box 25046, MS 939, Denver Federal Center, Denver, Colorado 80225, 303-236-2460, jdmccord@usgs.gov

Cynthia A. Rice, Box 25046, MS 939, Denver Federal Center, Denver, Colorado 80225, 303-236-1989, crice@usgs.gov