Analytical Techniques for Grade and Quality Control in Coal Mining

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XRD Application Specialist
Topics

Pulsed Fast & Thermal Neutron Activation (PFTNA)
Cross-belt Elemental Analysis of Coal

X-Ray Diffraction (XRD) & Computed Tomography (CT)
Phase and Structural Analysis of Coal

X-ray Fluorescence (XRF)
Elemental Analysis of Unashed Coal
Cross-belt Elemental Analysis of Coal
Introduction

- Coal is a high-volume commodity
- Continuous grading necessary to determine appropriate pricing and use
  - total moisture
  - inherent moisture
  - volatile matter
  - fixed carbon
  - ash content
  - total sulfur
  - calorific value
  - HGI
  - grain size
- Representative sampling is complicated and unreliable
- Cross-belt analyzers eliminate sampling difficulties by measuring the material on moving conveyor belts
- Cross-belt analyzers deliver “real-time” results, which can be used for process optimization
Introduction

- The majority of cross-belt analyzers are, in fact, neutron activation analyzers (NAA)
- Neutrons are used because:
  1. they are highly-penetrating particles, which means they can access large volumes of material (often through reinforced conveyor belts)
  2. they interact with atomic nuclei and induce characteristic gamma (γ) photon emissions, which are also highly penetrating and can, therefore, escape the sample and enter the detector
The principle

- (n,n')y reaction
  - Fast neutron → Inelastic scattering → Target nucleus
  - Prompt y emission

- (n,y) reaction
  - Thermal neutron → Absorption → Excited intermediate nucleus
  - Prompt y emission → Long-term relaxation
Cross-section

- The probability of interaction between neutrons and atomic nuclei is dependant on the so-called “neutron cross section”
  1. the target element
  2. the type of reaction (absorption, scattering, etc.)
  3. the incident particle energy
Sources

- The most common source of neutrons in cross-belt analyzers is the spontaneous fission of californium-252 by $\alpha$-decay:

  \[
  \begin{array}{c}
  _{98}^{252}\text{Cf} \rightarrow _{96}^{248}\text{Cm} + \alpha
  \\
  (\text{where } \alpha = 2p + 2n)
  \end{array}
  \]

- 70% of neutrons produced by this process have energies between 0.3 and 1.8 MeV and a maximum energy of approximately 6.5 MeV (low but detectable flux)

NO C AND O ANALYSIS!!!
Sources

- Neutron generators, like those used in our CNA³ Coal, offer significant advantages over isotope-based sources:
  1. pulsed 14 MeV neutrons via the fusion of deuterium and tritium
     \[ ^2_1H + ^3_1H \rightarrow n + ^4_2He \]
  2. programmable flux eliminates interruptive drift corrections and recalibrations and maintains precision
  3. the source can be switched off
  4. reduced import and export limitations and safety requirements
Electric Neutron Generator

**Diagram:**
- **Replenisher**
- **Ion Source**
- **Accelerating Gap**
- **Target**

**Equation:**
$$2^2H + 3^1H \rightarrow 4^2He + 1^0n$$

- **Deuterium**
- **Tritium**
- **Helium 4 Nucleus**
- **Fast Neutron (14 Mev)**

**On Demand Neutron Generation**
Safety

- Californium-252
  - 1.2 mSv/h

- Sodern Neutron Generator
  - natural background radiation
Coal analysis

- Real-time elemental analysis (H, C, N, O, Na, Al, Si, S, Fe, K, Ca, Ti & Mn – as received basis)
- Accurate calculation of:
  1. ash content
  2. moisture content
  3. calorific value
Example data

\[ Q = [145.44[C] + 620.28[H] + 40.5[S] - 77.54[O]] \]
CNA³ Coal positions
Benefits for power plants

- Improved combustion efficiency by approximately 0.4%
- Reduced boiler downtime and, therefore, production
  - reduced costs associated with oil restarts
  - reduced fines for non-production
- Reduced coal costs through accurate blending
- Reduced maintenance costs
  - elimination of sampling system
  - reduced corrosion and cokefaction in pipes
  - reduced downtime to remove slags

Payback estimated at 1.5 to 2 years
Phase and Structural Analysis of Coal
What is X-ray diffraction (XRD)?

- Versatile, nondestructive analytical technique
- Identification and quantitative determination of the various crystalline phases of compounds present in powdered and solid samples
- Quantification of the amorphous content
Mineral identification in coal

Fast phase ID of minerals in coal and coal related materials compared to microscopy

- Raw coal sample with high mineral content
  - Graphitic carbon (C)
  - Quartz (SiO$_2$)
  - Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$)
  - Calcite (CaCO$_3$)
  - Dolomite (CaMg(CO$_3$)$_2$)
  - Siderite (FeCO$_3$)
  - Anatase (TiO$_2$)

Organic material (mainly carbon)
None destructive analysis of the coal/ash ratio

Control erosion and abrasion of the mills by monitoring mineral content

- automatable
- operator independent
- non-destructive
- no chemicals required
- easy sample preparation

Mineralogical quantification of coal

- Determination of all crystalline phases in minutes
- Analysis of organic carbon (amorphous)
- Calculation of crucial process parameters such as total ash content
- No standards, monitors or calibrations needed

Kaolinite 56.4%
Calcite 0.6%
Dolomite 0.7%
Siderite 1.9%
Quartz 6.9%
Graphite 32.8%
Anatase 0.8%
Characterization of graphitic carbon

- Process of graphitization \( g \) (heat treatment) courses an increase in the degree of ordering within crystal structure of graphitic carbon
- Changes within lattice parameters \( d_{002} \) and crystallite size \( L_c \)
- \( d_{002} \) can be used as indicator for the graphitization \( g \)

Easy determination of crystallite size \( (L_c) \) and graphitization \( g \)

- Better performance of carbon materials (resistivity, conduction, thermal expansion, etc.) such as anodes for aluminium
CubiX³ Minerals

- Industrial diffractometer
- Fulfills modern international safety standards
- Dust protection for rough environments
- Analysis time of less then 5 minutes
- Handling of all common sample holder rings
- Ready for automation
Automation

- TWo INstruments
- One user interface
- XRF and XRD
- Belt connections
- Result via LIMS

- Robot automation
- Sample via airtube
- Automatic sample preparation
- Analytics
- Result via LIMS

- Container laboratory
- Sample preparation
- Analytics
- Result via LIMS
3D imaging - Computed tomography (CT)
Combined CT - XRD

- Computed Tomography (CT) as an analytical tool for material science has been mostly restricted to dedicated CT-instruments or large scale facilities
- We will demonstrate CT measurements on coal samples performed on an Empyrean multipurpose diffraction platform
Technical details
Technical details
Computed tomography (CT) on coal

Sample size: 12 x 12 x 8 mm

Mineral distribution

Pore size distribution

Mineral size distribution
Heat treatment of coal samples

- Samples were heat treated to simulate the char process
- Comparison of volume, void, composition changes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Room temperature</th>
<th>950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (mm)</td>
<td>5.4 x 6.6 x 11.2</td>
<td>4.8 x 5.9 x 10.1</td>
</tr>
<tr>
<td>Volume (mm³)</td>
<td>399.168</td>
<td>286.032</td>
</tr>
<tr>
<td>Shrink factor volume (%)</td>
<td>100.0</td>
<td>-28.336</td>
</tr>
<tr>
<td>Size (mm) [CT]</td>
<td>7.18 x 7.94 x 11.91</td>
<td>6.61 x 7.25 x 10.8</td>
</tr>
<tr>
<td>Volume (mm³) [CT]</td>
<td>353.1</td>
<td>287.51</td>
</tr>
<tr>
<td>Shrink factor (%) [CT]</td>
<td>100.0</td>
<td>-18.575</td>
</tr>
</tbody>
</table>
Density distribution

Coal with different densities = Colored

Inclusions/cracks = Black
Elemental Analysis of Unashed Coal

[Graph showing elemental analysis]
Coal is often graded and priced according to the concentration of sulfur, phosphorus, volatile materials and ash content.

Traditionally, the inorganic content has been quantified (often with XRF) by analyzing coal ash:
- Sample preparation is extremely time consuming.
- Multiple sample preparation steps introduce errors & contaminants.
Analysis process

Sampling → Drying → Crushing → Grinding → Splitting

Ashing → Addition of flux → Fusion → XRF analysis

Addition of wax → Press → XRF analysis
Application example

- **Procedure**
  1. coal standards acquired (Alpha & SABS)
  2. the standards were dried
  3. the standards were milled
  4. the standards mixed with wax
  5. the mixtures were pressed into pellets
  6. the standards were measured on an Epsilon 3

<table>
<thead>
<tr>
<th>Condition</th>
<th>Elements</th>
<th>kV</th>
<th>μA</th>
<th>Measurement Time (s)</th>
<th>Medium</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sr</td>
<td>30</td>
<td>300</td>
<td>60</td>
<td>Air</td>
<td>Ag</td>
</tr>
<tr>
<td>2</td>
<td>K, Ca, Ti, Fe &amp; Ba</td>
<td>12</td>
<td>600</td>
<td>60</td>
<td>Air</td>
<td>Al (thin)</td>
</tr>
<tr>
<td>3</td>
<td>Na, Mg, Al, Si, P &amp; S</td>
<td>6</td>
<td>1000</td>
<td>120</td>
<td>Helium</td>
<td>none</td>
</tr>
</tbody>
</table>
Spectrum examples

<table>
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<td>6</td>
<td>1000</td>
<td>120</td>
<td>Helium</td>
<td>none</td>
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Calibration examples

Calibration graph of S

Calibration graph of $\text{P}_2\text{O}_5$
## Calibration results

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration Range (wt%)</th>
<th>RMS (wt%)</th>
<th>LLD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0.014 – 0.29</td>
<td>0.0131</td>
<td>150</td>
</tr>
<tr>
<td>MgO</td>
<td>0.025 – 0.43</td>
<td>0.0111</td>
<td>100</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.86 – 11.27</td>
<td>0.1480</td>
<td>55</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.6 – 17.66</td>
<td>0.2810</td>
<td>45</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.007 – 0.14</td>
<td>0.0067</td>
<td>40</td>
</tr>
<tr>
<td>S</td>
<td>0.51 – 3.58</td>
<td>0.0764</td>
<td>10</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.029 – 0.215</td>
<td>0.0060</td>
<td>12</td>
</tr>
<tr>
<td>CaO</td>
<td>0.044 – 1.87</td>
<td>0.0232</td>
<td>8</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.06 – 0.63</td>
<td>0.0055</td>
<td>7</td>
</tr>
<tr>
<td>MnO</td>
<td>0 – 0.02</td>
<td>0.0006</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.147 – 3.815</td>
<td>0.0395</td>
<td>6</td>
</tr>
<tr>
<td>SrO</td>
<td>0.001 – 0.033</td>
<td>0.0010</td>
<td>2</td>
</tr>
<tr>
<td>BaO</td>
<td>0.004 – 0.042</td>
<td>0.0017</td>
<td>20</td>
</tr>
</tbody>
</table>
### Precision results

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Concentration (wt%)</th>
<th>1σ Standard Deviation (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.26</td>
<td>0.009</td>
</tr>
<tr>
<td>MgO</td>
<td>0.23</td>
<td>0.007</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.05</td>
<td>0.014</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.12</td>
<td>0.044</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.042</td>
<td>0.004</td>
</tr>
<tr>
<td>S</td>
<td>1.40</td>
<td>0.003</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.24</td>
<td>0.002</td>
</tr>
<tr>
<td>CaO</td>
<td>1.43</td>
<td>0.012</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.35</td>
<td>0.001</td>
</tr>
<tr>
<td>MnO</td>
<td>0.021</td>
<td>0.0003</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.75</td>
<td>0.004</td>
</tr>
<tr>
<td>SrO</td>
<td>0.014</td>
<td>0.0002</td>
</tr>
<tr>
<td>BaO</td>
<td>0.036</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Summary

- Accurate determination of ash, phosphorus and sulfur content is possible without time-consuming ashing procedures.

- Inexpensive solution for:
  1. mine/pit management
  2. stockpile sorting
  3. load-in control (specification checking)
  4. coal yard management
  5. blending