SAMPLING, CHARACTERIZATION, and ROUND-ROBIN ANALYSES OF DOMESTIC U.S. COAL-BASED RESOURCES CONTAINING HIGH RARE-EARTH ELEMENT (HREE) CONCENTRATIONS

DOE CONTRACT DE-FE0029007

DOE NETL Annual Project Review Meeting, April 9–11, 2019
Crosscutting, Rare-Earth Elements, Gasification Systems, and Transformative Power Generation

Chris J. Zygarlicke
April 10, 2019 Session C7: Process Economics & Embedded REE Demand
PROJECT DESCRIPTION

• **DOE NETL:** Vito Cedro and Mary Anne Alvin

• **Strategic alignment with DOE:** efficient rare-earth element (REE) resourcing and cost-competitive domestic supply, recovery, coal by-product utilization

• **Team**
  - University of North Dakota (UND) Energy & Environmental Research Center (EERC); UND Institute for Energy Studies (IES)
  - University of Kentucky (UK) Center for Applied Energy Research, the Kentucky Geological Survey (KGS) under the University of Kentucky Research Foundation, and Microbeam Technologies Inc. (MTI)
  - North Dakota Geological Survey (NDGS)

• **Partners:** Several U.S. coal mining companies and utilities

• **Contract:** October 2017 – September 2019
ACKNOWLEDGEMENT

- Kentucky Geological Survey (KGS)
- North Dakota Geological Survey (NDGS)
- Mining Companies
  - North American Coal Company
  - Kiewit Mining Group
  - Westmoreland Coal Company
  - BNI Coal Company
  - Leonardite Products LLC
  - Alliance Coal Company
  - Blaschak Coal Company
PROJECT OBJECTIVES

• Determine sources of coal and coal-related materials >= 300 parts per million (ppm) REEs as removed from the ground.
• Identify/review sample collection, preparation, and handling methods and acquire samples.
• Conduct advanced characterization on sample subsets for better understanding of modes of occurrence.
• Perform a round-robin interlaboratory study (RRIS) to determine the lab-to-lab and method-to-method variability in the REEs.
• Provide DOE NETL data for upload to NETL EDX.
PROJECT SAMPLING LOCATIONS

Coal Sources and Samples

Western Coal and North Dakota Lignite Emphasis
PROJECT UPDATE

D1 Updated Project Management Plan
D2 Final Sampling Plan
D3 Final Sample Preparation and Characterization Plan
D4 Sampling and Characterization Information
D5 Final RRIS Plan
D6 Interim Report – Sampling and First-Pass Characterization Across All Bulk Parent Materials
D7 Laboratory Analyses and Statistical Analysis Data
D8 Technical Progress Reports
D9 Technical Status Updates by Phone
D10 Final Report

M1 Complete Field Sampling
M2 Complete Sample Preparation and Characterization of All Bulk Parent Materials
M3 Complete Interim Report Based on Sampling and First-Pass Characterization Across All Bulk Parent Materials
M4 Complete Sample Preparation and Characterization of All Materials
M5 Complete Final Project Report
M6 Complete Sample Preservation for Retention (storage)
STANDARD AND ADVANCED METHODS

• Methods
  – REEs:
    ♦ UND digesting and analysis using ASTM Method D4503 including inductively coupled plasma–mass spectrometry (ICP–MS)
    ♦ UK-CAER ASTM D6357-11 using a combination of ICP–MS and ICP–OES (optical emission spectroscopy)
• Advanced characterization to aid in mode of occurrence evaluation:
  – FESEM, TEM, chemical fractionation characterization of REE-rich particles
  – New CCSEM method for REEs
  – Gravity separation for separating and concentrating REE-rich fractions
PROJECT RESULTS – SAMPLE COLLECTION

• Acquired coal and coal-related samples nonexistent, underrepresented, or having incomplete information in current databases.
• Contracted for 582 samples, collected over 600 representing 12 unique locations that span six major coal basins.
• UND and NDGS sampled western coal basins.
• UK-CAER and KGS sampled eastern U.S. coal basins.
• Non-coal: fly ash, bottom ash, acid mine drainage, clay-shale partings, and roof rock.
Sampling Effort
FINAL SAMPLE TOTALS AND TREEs

• Samples
  – 648 samples
    ♦ 560 from western resources
    ♦ 88 from eastern resources
    ♦ 46 samples are ash/AMD

• TREEs >= 300 ppm dry ash basis
  – 240 coal samples
  – 259 coal-ash samples

• TREEs >= 300 ppm dry mass basis
  – 21 coal samples
  – NOTE: 97 samples had levels >200 ppm
• 25–30 B tons lignite recoverable from world’s largest lignite deposit 350 B tons
• ~30 M tons/yr lignite used; 800-year supply
• Mature coal utilization infrastructure, top 10 coal producer, supplies 66% of ND electricity, Project Tundra FEED study for commercial CO₂ capture.
• 3 major coal zones; Beulah-Zap, Hagel, Harmon-Hanson (mining of this lignite ceased in 1995)
• 7 lignite-fired power plants > 4000 MWe total capacity.
HARMON–HANSON LIGNITE POTENTIAL

- Outcrops of the Harmon, Hanson, and H bed seams, Fort Union Group, in SW North Dakota
- 6–20’ accessible seams, former mining operations
- 144 samples collected
- Upper seams show markedly higher TREEs; Harmon–Hanson ~400 ppm and H Bed >1000 ppm dry coal basis.
HARMON–HANSON SAMPLING LOCATION

Harmon–Hanson lignite at top of outcrop

Thin 16-inch H-Bed does not occur here
FREEDOM MINE – BEULAH–ZAP LIGNITE

- Active stable mine-mouth operations of North American Coal Co. with good potential for lower cost extraction
- Lignite from Twin Buttes and Beulah–Zap seams
- Beulah–Zap 18 to 22’ seams
- Twin Buttes 6’ seams with 25–30’ of overburden where actively mined
- 93 samples were collected.
- Limited >300-ppm samples, but show high HREE/LREE ratio of 0.89

Photo: Star Tribune, AP Photo/James MacPherson
SAVAGE AND CENTER LIGNITES

• Savage (MT) lignite
  – Little existing characterization data
  – All REE levels <200 ppm (mass basis)
  – Indicators of volcanic ash deposits (rhyolitic glass) will be examined in samples near top of seam and near shale partings.

• Center (ND) lignite
  – 71 samples; several with >1 HREE/LREE, but TREEs <40 ppm
BUCKSKIN MINE – ANDERSON AND CANYON

• Powder River Basin in Wyoming and part of the Fort Union Group.
• The USGS CoalQual database showed several samples >200 TREEs; collected 80 coals and a few power plant ashes.
• Coals ranged from 10- to 210-ppm TREEs, with 17% avg. ash content
• Power plant fly ash/bottom ash samples >300-ppm TREEs
TEXAS GULF COAST COAL TARGETS

- Strip-minable ~4-Mtpy thin multiseam coal mines part of the Gulf Coast or Texas Lignite Basin
- San Miguel Mine – Jackson Coal (lignite) extensive mining infrastructure, 12 samples averaging 125-ppm TREEs.
- Sabine Mine – 4 Mtpy, Wilcox lignite, ten samples averaging ~45-ppm TREEs.
- Eagle Pass Mine – Olmos Coal, (subbitum.) and two out of 28 samples had ~350-ppm TREEs dry mass basis.

Photo: William Luther/San Antonio Express-News
SELECT WESTERN SAMPLES >300-PPM TREES, PPM DRY SAMPLE BASIS

<table>
<thead>
<tr>
<th>Description</th>
<th>Seam</th>
<th>State</th>
<th>Total REEs</th>
<th>HREE/L REE</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite, Outcrop, Upper Seam</td>
<td>Harmon</td>
<td>ND</td>
<td>439</td>
<td>0.46</td>
<td>28</td>
</tr>
<tr>
<td>Lignite, Outcrop, Lower Seam</td>
<td>Harmon</td>
<td>ND</td>
<td>261</td>
<td>0.44</td>
<td>21</td>
</tr>
<tr>
<td>Lignite, Outcrop, Top Seam</td>
<td>Hanson</td>
<td>ND</td>
<td>370</td>
<td>0.38</td>
<td>39</td>
</tr>
<tr>
<td>Lignite, Outcrop, Top Seam</td>
<td>H bed</td>
<td>ND</td>
<td>1024</td>
<td>0.20</td>
<td>60</td>
</tr>
<tr>
<td>Lignite, Outcrop, Lower Seam</td>
<td>H bed</td>
<td>ND</td>
<td>345</td>
<td>0.33</td>
<td>92</td>
</tr>
<tr>
<td>Lignite, Freedom Mine</td>
<td>Twin Butte</td>
<td>ND</td>
<td>365</td>
<td>0.89</td>
<td>30</td>
</tr>
<tr>
<td>Fly Ash, Subitum., Buckskin Mine</td>
<td>Anderson</td>
<td>WY</td>
<td>403</td>
<td>0.36</td>
<td>NA</td>
</tr>
<tr>
<td>Bottom Ash, Subitum., Buckskin Mine</td>
<td>Anderson</td>
<td>WY</td>
<td>343</td>
<td>0.39</td>
<td>NA</td>
</tr>
<tr>
<td>Subitum., Buckskin Mine</td>
<td>Anderson</td>
<td>WY</td>
<td>10–210</td>
<td>0.25–0.50</td>
<td>6–75</td>
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<tr>
<td>Eagle Pass (A1 P301C) BU – coal</td>
<td>Olmos</td>
<td>TX</td>
<td>340</td>
<td>0.34</td>
<td>49</td>
</tr>
<tr>
<td>Eagle Pass (A1 P301C) B IB middle – coal</td>
<td>Olmos</td>
<td>TX</td>
<td>315</td>
<td>0.26</td>
<td>91</td>
</tr>
</tbody>
</table>
EASTERN U.S. (APPALACHIAN) RESULTS

• 10% of project samples (88) collected from eastern U.S. coal mines and processing plants
  – 12 Pennsylvania bituminous
  – 18 Pennsylvania anthracite – Llewellyn
  – 26 East Kentucky bituminous
  – 32 Alabama bituminous
• 12 ash/AMD samples
• No coal samples >300 ppm TREEs, mass basis
• 69 samples > 300 ppm TREEs ash basis

4-AMD (acid mine water, sludge) Central Appalachian Eastern Kentucky
1-AMD (sludge and coal fines) Northern Appalachian, Pennsylvania Anthracite
# EASTERN SAMPLES >300-PPM TREES, PPM DRY MASS BASIS

<table>
<thead>
<tr>
<th>Description</th>
<th>Seam</th>
<th>State</th>
<th>Total REEs Y + Sc</th>
<th>HREE/LREE</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous, Carb. Shale</td>
<td>Pottsville</td>
<td>AL</td>
<td>317</td>
<td>0.24</td>
<td>89</td>
</tr>
<tr>
<td>Bituminous, Roof Rock</td>
<td>Pottsville</td>
<td>AL</td>
<td>537</td>
<td>0.29</td>
<td>94</td>
</tr>
<tr>
<td>Bituminous, Fly Ash/FGD</td>
<td>Breathitt</td>
<td>KY</td>
<td>326</td>
<td>0.50</td>
<td>86</td>
</tr>
<tr>
<td>Bituminous, Bottom Ash</td>
<td>Breathitt</td>
<td>KY</td>
<td>392</td>
<td>0.35</td>
<td>69</td>
</tr>
<tr>
<td>Bituminous, Fly Ash</td>
<td>Breathitt</td>
<td>KY</td>
<td>653</td>
<td>0.44</td>
<td>96</td>
</tr>
<tr>
<td>Bituminous, Stoker Ash</td>
<td>Breathitt</td>
<td>KY</td>
<td>776</td>
<td>0.37</td>
<td>96</td>
</tr>
</tbody>
</table>
- Underrepresented southern Appalachian bituminous coal region
- Sampling from southeast edge of Alabama Black Warrior Basin
- Hydrothermal metamorphism with potential for high TREE contents.
- 20/32 coals >300 ppm TREEs on ash basis, highest at ~570 ppm.
RESULTS – REE TRENDS IN LOW-RANK COALS

- Twofold focus of sampling: 1) maximize samples >300 ppm and 2) learn more about modes of occurrence and trends of distribution for future reserve estimation and extraction methods.
- Larger quantities of REEs followed literature observations concentrating near top and bottom of seam.
- Laterally, some spatial data to verify TREE quantities from hundreds of yards to a few miles.

Gascoyne Mine, Harmon lignite seam, 1985
HREE/LREE VERSUS TREE – ALL COAL SAMPLES

300 ppm

HREE/LREE = 1
RESULTS -- CCSEM METHOD DEVIRED FOR DETECTION AND QUANTIFICATION OF REEs IN COALS AND ASH

- Hitachi high-magnification FESEM
- Particle keV translated to chemical typing and standards
- Small particles and associated chemistries can be differentiated
Low-rank coals will have abundant alkali in association with organic functional groups.
HITACHI FE SEM

- Automated detection, identification, and quantification of REE-rich phosphate particles in coal
- A significant fraction of the REEs associated in the organic structure in the coal
- Very fine bright spots are La, Ce, Nd, Gd particles

From the H- Bed Lignite Sample, Slope County Southwestern ND
<table>
<thead>
<tr>
<th>Description</th>
<th>% Ash, dry</th>
<th>Total REE + Y + Sc, ppm (dry coal)</th>
<th>HREE/LREE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND Lignite – Hanson</td>
<td>39</td>
<td>370</td>
<td>0.38</td>
</tr>
<tr>
<td>ND Lignite – H-Bed</td>
<td>60</td>
<td>1026</td>
<td>0.2</td>
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<tr>
<td>ND Lignite – H-Bed</td>
<td>26</td>
<td>398</td>
<td>0.35</td>
</tr>
<tr>
<td>ND Lignite – Twin Butte</td>
<td>30</td>
<td>365</td>
<td>0.89</td>
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<tr>
<td>ND Lignite – Hagel</td>
<td>29</td>
<td>233</td>
<td>0.45</td>
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<tr>
<td>ND Lignite – Harmon</td>
<td>28</td>
<td>439</td>
<td>0.46</td>
</tr>
<tr>
<td>TX Lignite – Olmos</td>
<td>21</td>
<td>257</td>
<td>0.32</td>
</tr>
<tr>
<td>WY Subbit. – Anderson</td>
<td>21</td>
<td>189</td>
<td>0.34</td>
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<tr>
<td>MT Lignite – Pust</td>
<td>54</td>
<td>150</td>
<td>0.85</td>
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<tr>
<td>KY Bitum.</td>
<td>6</td>
<td>126</td>
<td>0.3</td>
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</tbody>
</table>
RESULTS – STATUS OF THE RRIS

- Sample materials and specific round-robin instructions have been assembled.
- Sample info was sent in January 2019.
- Results due March 29, 2019.
- Four coals, three fly ash, clay parting, shale, anthracite AMD, and mine waste
- Three samples are NIST SRMs.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Origin</th>
<th>~TREE, ppm, dry mass basis</th>
<th>~ Ash Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite coal</td>
<td>North Dakota/Harmon Seam</td>
<td>400</td>
<td>25–30</td>
</tr>
<tr>
<td>Subbituminous coal</td>
<td>Wyoming/Powder River Basin</td>
<td>200</td>
<td>20–22</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>Central Appalachian</td>
<td>125</td>
<td>6–8</td>
</tr>
<tr>
<td>Bituminous fly ash</td>
<td>Kentucky power plant/Central Appalachian coal</td>
<td>700</td>
<td>98–100</td>
</tr>
<tr>
<td>Subbituminous fly ash</td>
<td>Wisconsin power plant/Powder River Basin coal</td>
<td>400</td>
<td>98–100</td>
</tr>
<tr>
<td>Clay parting</td>
<td>Texas/subbituminous</td>
<td>280</td>
<td>95–98</td>
</tr>
<tr>
<td>Acid mine drainage sludge</td>
<td>Pennsylvania/Central Appalachian anthracite</td>
<td>200</td>
<td>50–55</td>
</tr>
<tr>
<td>Bituminous fly ash</td>
<td>NIST SRM – Pennsylvania power plant/bituminous</td>
<td>&gt;600</td>
<td>90–93</td>
</tr>
<tr>
<td>Shale</td>
<td>USGS SRM – Pennsylvania Bush Creek shale</td>
<td>315</td>
<td>90–93</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>NIST SRM – Pennsylvania bituminous</td>
<td>50</td>
<td>6–8</td>
</tr>
<tr>
<td>Mine waste material</td>
<td>NIST SRM – Central Colorado</td>
<td>200</td>
<td>88–90</td>
</tr>
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</table>

1 To be determined
2 Added after Final RRIS Plan was submitted. Pending approval from DOE.
RRIS PARTICIPATING LABORATORIES

- 15 laboratories
- Statistical analysis of reported data:
  - **Repeatability** (within laboratory variability)
  - **Reproducibility** (between laboratory variability)
  - **Bias** (deviation from known values of standard reference materials)
  - **Variability** (Method to method)

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Accreditation/Certification</th>
<th>Procedure Method D6357-11</th>
<th>Procedure Method D4503-08</th>
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<tr>
<td>Act Labs</td>
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<tr>
<td>Duke University</td>
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<tr>
<td>Geochemical Testing, Inc.</td>
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<td>Hazen Research, Inc.</td>
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<tr>
<td>Kentucky Geological Survey</td>
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<td>McCreath Laboratories</td>
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<tr>
<td>Nexus Geos/University of Nebraska (Tetra Tech)</td>
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<td>X</td>
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<tr>
<td>Ohio State University</td>
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<td>Research Triangle Institute</td>
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<td>Standard Laboratories, Inc.</td>
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<td>University of Iowa</td>
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<td>UND-EERC</td>
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<tr>
<td>Southern Research - Water Research Center</td>
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<td>X</td>
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<tr>
<td>University of Missouri Research Reactor Center</td>
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<td>NAA</td>
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</tbody>
</table>
INSIGHTS: INDUSTRY, MARKETS, NEEDS

- New potential resources for REEs and information on the association of these REEs in coal beds could impact future new domestic markets
- 648 samples mostly from western resources and specific focus on ND lignite
- 259 samples with TREEs $\geq$ 300 ppm dry ash basis
- All but one of the western sources have existing mine infrastructure and energy utilization
INSIGHTS: INDUSTRY, MARKETS, NEEDS

• Western low rank coals
  – Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.

• Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.

• Data for estimation of regional REE reserves (ongoing)

• Critical mode of occurrence and association determinations may help devise methods for economic extraction.
CONCLUDING REMARKS

• Nearly 650 samples of coal and coal-related materials examined as potential new sources of high REEs; a strategic goal of DOE.
• Confirmation of REE economic potential in select ND lignites and southern Appalachian bituminous coals.
• Remaining contract milestones/deliverables: complete all characterization, complete final report, and provide quality data set for DOE NETL EDX.
• On target progress of a round robin interlaboratory study for the preparation and analysis of REE bearing materials to aid in accurate REE resource assessments and commercial development.
• Advanced SEM methods developed and demonstrated to aid in designing better REE identification, quantification, and extraction.
CONVENTIONS

• HREE: heavy rare earth element
• LREE: light rare earth element
• Scandium is not used in the HREE/LREE ratio calculation.
• TREEs: total rare-earth elements (includes Sc + Y)
TREE VERSUS ASH CONTENT (all samples)
NEXT STEPS – GRAVITY SEPARATIONS AND FINISH ALL CHARACTERIZATION

• Strategic selection of ten samples for float–sink separation to evaluate concentration impacts; aid in mode of occurrence determination, and gain insights on extraction/recovery.

• In low-rank coals, REEs are concentrated in the organic fraction, so by removing the higher-density, mineral-rich fraction of the coal, the REEs can be substantially enriched in the remaining organic-rich fraction.

• In high-rank coals, the REEs are concentrated in the higher-density mineral matter.

• The float–sink techniques to be used are outlined in ASTM D4371 (2012) Standard Test Method for Determining the Washability Characteristics of Coal.

• The separations will be done by a commercial lab (TBD).

• Characterization is pending for gravity fractions.
INSIGHTS: INDUSTRY, MARKETS, NEEDS

• Western low rank coals
  – Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.
• Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.
• Data for estimation of regional REE reserves (ongoing)
• Critical mode of occurrence and association determinations may help devise methods for economic extraction.
INSIGHTS: INDUSTRY, MARKETS, NEEDS

• Western low rank coals
  – Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.
  – The value of samples with TREEs >300 that show a HREE/LREE ratio > 1, may need further clarification, since very few samples fit this criteria in the study.

• Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.

• Estimation of regional REE reserves (ongoing) holds promise for potential new reserves.

• Critical mode of occurrence and association determinations may help devise methods for economic extraction.