

DOE Critical Minerals & Materials

Domestic Wastes and Byproducts – A Resource for Critical Material Supply Chains

Evan J. Granite United States Department of Energy

Alaska Core-CM Stakeholders Meeting

September 2023

"Dynamic Dozen" Critical Materials

100% clean electricity by 2035: 30 GW offshore wind by 2030
Zero-emission transportation: 50% EV adoption by 2030

 <u>Neodymium</u>, <u>Praseodymium</u> and <u>Dysprosium</u> for magnets

G

0

- <u>Lithium</u>, <u>Cobalt</u>, <u>Nickel</u>, <u>Graphite</u>, and <u>Manganese</u> for energy storage
- Iridium & Platinum for electrolyzers; Platinum for fuel cells
- <u>Gallium</u> for wide bandgap semiconductors, LEDs
- <u>Germanium</u> for microchips (semiconductors)

- Magnets enable efficient electric machines including wind generators, electric and fuel cell vehicle motors, industrial motors
- Batteries are needed for electric vehicles and grid storage to enable high penetration of zero-emission transportation and intermittent clean power generation
- Iridium and platinum for electrolyzers are needed for green hydrogen production and platinum for fuel cells used in transportation and stationary energy storage.
- Wide bandgap power electronics enable high voltage power generation (like wind) to connect to the grid
- Microchips for sensors, data, and control play an important role in SMART manufacturing, which will be needed to increase efficiency and minimize waste (inclusion GHGs); Fiber and infrared optics

America's Strategy to Secure the Supply Chain for a Robust Clean Energy Transition

Introducing The Electric Eighteen

Critical Materials for Energy

- Aluminum
- Cobalt
- Copper
- Dysprosium
- Electrical Steel* (grain-oriented steel, non-grain-oriented steel, and amorphous steel)
- Fluorine
- Gallium
- Iridium
- Lithium
- Magnesium
- Natural Graphite

Introducing The Electric Eighteen

Critical Materials for Energy

- Neodymium
- Nickel
- Platinum
- Praseodymium
- Silicon
- Silicon Carbide
- Terbium
- "Critical Materials Assessment", USDOE, July 31, 2023, available on-line <u>https://www.energy.gov/sites/default/files/2023-07/doe-critical-material-assessment_07312023.pdf</u>

Characteristics of Wastes and Byproducts of Interest

- Voluminous
- Preferably Currently Produced
- Accessible
- Opportunities for Environmental Remediation
- Known and Elevated Concentrations of Critical & Valuable Elements
- Known pH Data for Extraction of CM (acidic) or Carbon Dioxide Capture (basic)
- Preferably Easily Extractable
- Multiple Salable Products
- Critical Materials Are Concentrated In Many Wastes and Byproducts

Potential Wastes and Byproducts of Interest



- Coal, Waste Coal, Acid Mine Drainage Many Critical Materials
- Ash Impoundments Many Critical Materials
- Petroleum Refinery Wastes (Desalter, Coke) Ni, V, Mo heavy crudes
- Steel Slag
- Red Mud (Bauxite Residue) Rare Earths
- Smelters Many Critical Materials Within Flue Dust and Slags
- Mine Tailings Many Critical Materials
- Asbestos
- Produced Waters from Oil and Gas Production Lithium
- Municipal Solid Waste Source of Critical Materials
- Municipal Sludge Potential Source of Platinum Group Metals
- E-Waste Source of Platinum Group Metals and Critical Materials

Potential Wastes and Byproducts of Interest



- Coal, Acid Mine Drainage Pilot Efforts (FECM)
- Ash Impoundments Treasure Chest of Critical Elements, Pilots (FECM)
- Petroleum Refinery Wastes (Desalter, Coke) FECM, USGS, CANMET
- Steel Slag
- Smelters Ores Can Contain Critical Elements <u>Heat is our Friend !</u>
- Mine Tailings Ores Can Contain Critical Elements
- Red Mud Can Contain 0.1 1% Rare Earths
- Asbestos
- Produced Waters New Efforts Within FE & EE
- Municipal Solid Waste 1 ton/person/ per year estimated 1- 17 wt.% metals
- Municipal Sludge Great Excitement in 2015, ES&T Paper Valuable Metals
- E-Waste Platinum Group Metals, Nickel, Lithium, Cobalt



Concentration of Critical Metals

- Coal Combustion Fly Ash and Bottom Ash
- MSW Energy Recovery/Incineration Fly Ash and Bottom Ash
- Sewage Sludge Incineration Fly Ash and Bottom Ash
- Smelter Flue Dusts
- Steel Slags
- Petroleum Refinery Cokes and High Boiling Distillation Fractions
- Volatility Melting and Boiling Points of Elements and Compounds
- Critical Elements Typically Concentrate in High Temperature Products
- Ashes, Flue Dusts, Slags, Cokes and High Boiling Fractions
- Happy Accident !
- Heat Concentrates CM in Numerous Abundant Solid Wastes "Granite Equation"

Average Concentrations in Domestic Coal



- Nd 9.5 ppm (COALQUAL analysis Lin, Granite)
- Dy 3.39 ppm (COALQUAL analysis Lin, Granite)
- Li 16 ppm (Finkelman 2018)
- Co 6.1 ppm (Finkelman 2018)
- Ni 14 ppm (Finkelman 2018)
- Ir 0.002 ppm (World Coal Lin, Granite 2018)
- Pt 0.035 ppm (World Coal Lin, Granite 2018)
- Ga 5.1 ppm (Lin, Granite 2018)
- Ge 7.2 ppm (Lin, Granite 2018)

Rough Quantities in US Legacy Waste Coal (OME)



- Nd 38,000 tons
- Dy 13,600 tons
- Li 64,000 tons
- Co 24,400 tons
- Ni 56,000 tons
- Ir 8 tons
- Pt 140 tons
- Ga 20,400 tons
- Ge 28,800 tons
- Within Four Billion Tons of Waste Coal, Scattered Across 1,000 Sites



- Nd 86 ppm
- Dy 31 ppm
- Li 144 ppm
- Co 55 ppm
- Ni 126 ppm
- Ir 0.02 ppm
- Pt 0.3 ppm
- Ga 10 ppm
- Ge 65 ppm

Rough Quantities in US Legacy Coal Ash (OME)



- Nd 172,000 tons
- Dy 62,000 tons
- Li 288,000 tons
- Co 110,000 tons
- Ni 252,000 tons
- Ir 40 tons
- Pt 600 tons
- Ga 20,000 tons
- Ge 130,000 tons
- Within Two Billion Tons of Ash, Scattered Across Over 1,300 Sites

Potential Supply in US Legacy Coal Ash, At Current Rates of Consumption



~ 40-year supply (estimate)

~ 14-year supply (estimate)

130-year supply

15-year supply

1.1-year supply

15-year supply

15-year supply

- Nd 172,000 tons
- 62,000 tons • Dy
- Li 288,000 tons
- 110,000 tons Co
- Ni 252,000 tons
- Ir 40 tons
- Pt 600 tons
- 20,000 tons • Ga
- 1,100-year supply 130,000 tons 3,900-year supply • Ge
 - U.S. Geological Survey, 2022, Mineral Commodity Summaries

Next Steps



Producing Estimates on Extent of Potential Resource

- Petroleum Refinery Wastes (Desalter, Coke)
- Steel Slag
- Red Mud
- Smelters
- Mine Tailings
- Asbestos
- Produced Waters
- Municipal Solid Waste
- Municipal Sludge
- E Waste
- Preparing Reports and Notes for Journals



- Approximately 300 Million Tons/Year ~ 1 ton/year/person
- "8 % metals" Crude Composition EPA (yard waste, food, paper, cardboard, plastics, wood, metals,...)
- Really ~ 1 17% metals (other waste categories contain embedded metals)
- Unfortunately Includes Some E Wastes
- A Great Opportunity for CMs
- Landfills
- MSW Incinerator (Energy Recovery) Ashes
- <u>https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/</u> <u>national-overview-facts-and-figures-materials</u>
- <u>https://archive.epa.gov/epawaste/nonhaz/municipal/web/html/</u>
- EPA and Literature for Detailed Compositions

Municipal Sewage Sludge



- Excitement on PGM Contents ~ ppm levels Pt, Pd, Rh
- Source Road Dusts Catalytic Converters
- Significant Literature on PGMs in Sewage Sludge
- Yale 2015 ES&T
- Quantities and Processing of Sewage
- <u>https://www.epa.gov/biosolids/basic-information-about-biosolids</u>
- <u>https://www.epa.gov/biosolids/sewage-sludge-surveys</u>
- <u>https://www.epa.gov/sites/default/files/2021-04/documents/tnsss-appendix-elemental-analyses-report.pdf</u>
- EPA and Literature for Detailed Compositions





- Voluminous Byproduct of Aluminum Production
- Stoichiometry of Bayer Process
- 1 2 Times as Much Red Mud Produced versus Alumina
- USGS Statistics Aluminum Production (USGS Mineral Commodity Summaries 2022)
- ~ 1.1 Million Tons Aluminum Produced in US in 2021
- Sodium Hydroxide Bauxite Ore
- Highly Alkaline
- Enriched in Rare Earths 0.1 1 % by weight
- Perhaps Enough to Supply Annual US Demand for Rare Earths (10,000 tons/year)
- A Fantastic Opportunity for RE and Carbon Dioxide Capture/Sequestration
- At Least 10% of Annual US Demand, From Currently Produced Red Mud
- Additional Rare Earths from Legacy Impoundments
- Current ARPA-E Research Doug Wicks from DOE





- Approximately 90 million tons Steel Produced/year in US
- Recent Thesis Recover Valuable Elements from Slag
- "Sustainable Valorization of Steelmaking Slag: From Metal Extraction to Carbon Sequestration", PhD Thesis, Jihye Kim, Department of Chemical Engineering and Applied Chemistry, University of Toronto, 2021
- Obtaining Slag Compositions and Production Statistics

Petroleum



- Refine Approximately 18 Million barrels Petroleum/Day in US (USDOE EIA)
- Heavy Crudes Contain Valuable Metals
- Roughly 1/3 US Crudes are "Heavy"
- Nickel, Vanadium and Molybdenum
- Other Valuable Metals are Present as Well (PGMs, Co)
- Concentrations up to 500 ppm V, 20 ppm Ni, 1 ppm Mo
- Concentrate in the Petroleum Coke at Refinery
- "Processing of Petroleum Coke for Recovery of Vanadium and Nickel", Hydrometallurgy, P.B. Queneau, R.F. Hogsett, L.W. Beckstead, D.E. Barchers, 22(1-2), 3-24, 1989
- EIA, USGS, CANMET, Exxon-Mobil & NIST for Detailed Petroleum Compositions

E - Wastes



• Computers, Televisions, Phones,

Crude Compositions:

- Cu 15%,
- Al 4.7%
- Fe 3.1%
- Pb 2.8%
- Sn 1.8%
- Ni 1.6%
- Zn 1.2%
- Ag 0.06%
- Au 0.03%

"Bio-extraction of precious metals from urban solid waste", AIP Conference Proceedings 1805, 020004 (2017); https://doi.org/10.1063/1.4974410, Published Online: 20 January 2017 Subhabrata Das, Gayathri Natarajan and Yen-Peng Ting

• EERE and EPA for Volumes & Detailed Compositions



- Flue Dusts
- Slags
- Extensive Literature for Copper, Zinc, Nickel
- USGS Statistics on Domestic Production (2023 Mineral Commodity Summaries)
- Developing Estimates

Mine Wastes



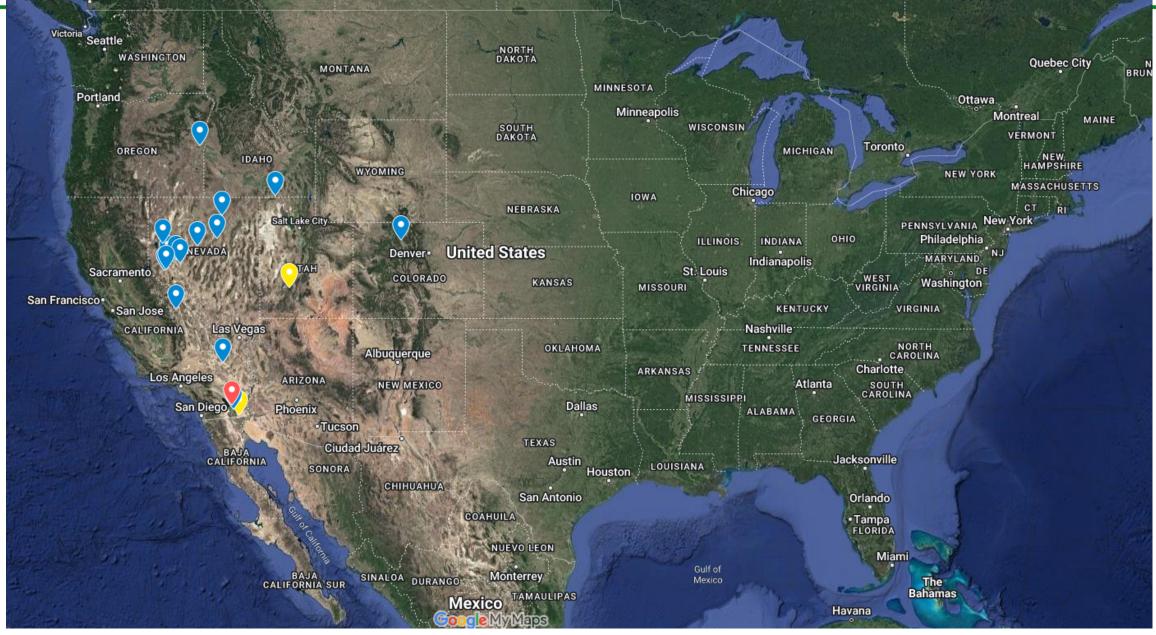
- Domestic High-Quality Ores Depleted over Time
- Cut-Off Grades for Most Metals have been Reduced
- Many Mine Tailings and Waste Rocks Now Contain Economically Recoverable Concentrations of Metals
- Tailings, Waste Rock
- Rock Ore Ratio (USGS) Publications
- USGS
- Peer-Reviewed Literature, Especially for Cu, Zn, Ni
- Rio Tinto Efforts to Recover Tellurium and Copper from Mine Wastes and Tailings
- Developing Estimates



- Enormous Quantities 20 25 billion barrels produced water/year in US
- USGS Database on Produced Waters
- Engle, M. A., Saraswathula, V., Thordsen, J. J., Morrissey, E. A., Gans, K. D., Blondes, M. S., Kharaka, Y. K., Rowan, E. L., & Reidy, M. E. (2019). U.S. Geological Survey National Produced Waters Geochemical Database v2.3 [Data set]. U.S. Geological Survey. <u>https://doi.org/10.5066/F7J964W8</u>
- "Incomplete"
- Literature
- Lithium is a Focus
- Leachates from Waste Impoundments
- Possibilities for CMs (FECM)
- DOE to Invest More Than \$18 Million to Treat Wastewater, Recover Valuable Minerals
 - Announcement 2/10/23 https://netl.doe.gov/node/12321

USGS Data Produced Waters and Brines - Lithium







- <u>Domestic Sources of Li Google My Maps</u> Blue < 20 ppm, Yellow 20 80 ppm,
- Red > 80 ppm Lithium, Courtesy of Naomi Akiyama
- Lithium extraction from oilfield brine, Pamela Daitch, University of Texas at Austin, MS Thesis, 2018. <u>Lithium extraction from oilfield brine (utexas.edu)</u>
- The U.S. Geological Survey National Produced Waters Geochemical Database was utilized to identify lithium-rich brine from wells across the U.S. The volume and concentration potential of the most promising lithium-enriched geologic formation were calculated.
- Advanced technology offers the advantage of recovering Li from concentrations as low as 70 mg/L. Of the produced water samples, only 344 samples had Li concentrations greater than or equal to 70 mg/L.



Outer Space

 Recent Dissertations on Meteorites, Asteroids, Moon, and Mars as Sources of Critical Materials – NASA is Part of Intergovernmental Efforts Led by DOE – "Space Mining"

Ocean Floor

• Seabed Minerals – DOE Leading This Effort

Arctic Region

• <u>www.arctic.gov</u> Challenging Region – but See Others

Ocean Waters

- A Long-Held Dream Quantities Enormous, But Concentrations are Low
- Example Lithium 1 ppm
- Could Co-Production of Metals and Potable or Useable Water Aid Economics?

Ash Impoundment Leachates

• Digested/Extracted Materials ala Acid Mine Drainage Efforts

Other Non-Traditional Sources



Garnet Abrasives and Sands

- Garnet Used as Industrial Abrasives
- Approximately 100,000 tons Produced Annually in United States
- Recent Papers from Oak Ridge and Jacobs University in Germany
- Suggest High Rare Contents As Much as 0.1 1% by Weight Total REY+ Sc
- Particularly for Heavy Rare Earths and Scandium
- Unfortunately, Extraction Seems Difficult
- "Potential of garnet sand as an unconventional resource of the critical high-technology metals scandium and rare earth elements", Franziska Klimpel, Michael Bau, Torsten Graupner, Scientific Reports, 11:5306, 2021
- "Industrial garnet as an unconventional heavy rare earth element resource: Preliminary insights from a literature survey of worldwide garnet trace element concentrations", N. Alex Zirakparvar, 2022, Ore Geology Reviews, in press, available on-line, July 22, 2022



Phosphogypsum

- Rare earths are often found in nature as the phosphate monazite
- •
- Phosphogypsum wastes are byproducts of phosphoric acid or fertilizer production
- Much of the original rare earth elements originally present with the phosphate rocks are concentrated in the phosphogypsum
- DOE-supported research is currently examining the potential of these wastes for recovery of the rare earths

Acknowledgements



- Brent Sheets
- Arctic Energy Office (Givey Kochanowski, Michael McEleney, Erin Whitney, and Carolyn Hinkley)
- Grant Bromhal
- Jen Wilcox
- Mary Anne Alvin
- Anna Wendt
- Helena Khazdozian
- FECM Julia Pizzutti, Gabe Hernandez
- Brad Crabtree
- Doug Wicks
- Kavita Vaidyanathan
- Lisa Friedersdorf
- Naomi Akiyama and USDOE Mickey Leland Energy Fellowship Program

Questions



• <u>evan.granite@hq.doe.gov</u>

References



- "Domestic Wastes and Byproducts: A Resource for Critical Material Supply Chains", Evan Granite, Grant Bromhal, Jen Wilcox, Mary Anne Alvin, National Academy of Engineering, The Bridge, 53(3), Fall 2023
- Potential Resources From Abundant Domestic Wastes, Byproducts and Non-Traditional Sources, Evan Granite, DOE Critical Minerals & Materials Workshop, Alaska Pacific University, February 22, 2023, available on-line: <u>https://www.energy.gov/sites/ default/files/2023-04/doe-critical-minerals-materials-potential-resources-fromabundant-domestic-wastes-byproducts-non-traditional-sources.pdf</u>
- "Recovery of Rare Earth Elements and Critical Materials from Coal and Coal Byproducts", Report to Congress, USDOE, May 25, 2022

References



- 1. "Leaching of Rare Earth Elements and Yttrium from a Central Appalachian Coal and the Ashes Obtained at 550-950°C", Ronghong Lin, Elliot Roth, Murphy Keller, Bret Howard, Yee Soong, Ping Wang, and Evan Granite, Journal of Rare Earths, 40(5), 807-814, May 2022.
- 2. "Chemistry of Trace Inorganic Elements in Coal Combustion: A Century of Discovery", Constance Senior, Evan Granite, William Linak, and Wayne Seames, Energy & Fuels, 34, 12, 15141-15168, 2020.
- 3. "Investigation of Thulium and other Rare Earth Element Concentrations in NIST 1632a Bituminous Coal Standard Reference Material" by Roth, Elliot; Bank, Tracy; Granite, Evan, Geostandards and Geoanalytical Research, 42(2), 263-269, June 2018.
- 4. "Evaluation of Rare Earth Elements and Yttrium in U.S. Coal Using the USGS COALQUAL Database Version 3.0", Ronghong Lin, Yee Soong, Evan Granite, International Journal of Coal Geology, 192, 1-13, 2018.
- 5. "Evaluation of Critical Elements in U.S. Coals Using the USGS COALQUAL Database Version 3.0", Ronghong Lin, Yee Soong, Evan Granite, International Journal of Coal Geology, 192, 39-50, 2018.
- 6. "Application of Sequential Extraction and Hydrothermal Treatment for Characterization and Enrichment of Rare Earth Elements from Coal Fly Ash", Ronghong Lin, Mengling Stuckman, Bret Howard, Yee Soong, Tracy Bank, Christina Lopano, Elliot Roth, Megan Macala, Evan Granite, Fuel, volume 232, 124-133, 2018.
- 7. "Effect of Pre-Reaction Ball Milling on Kinetics of Lanthanum Phosphate Roasting with Sodium Carbonate", Ward Burgess, Murphy Keller, Jonathan Lekse, Bret Howard, Elliot Roth, Evan Granite, Industrial & Engineering Chemistry Research, 57, 6088–6096, 2018.
- 8. "Distribution and Speciation of Rare Earth Elements in Coal Combustion By-Products via Synchrotron Microscopy and Spectroscopy", Mengling Stuckman, Christina Lopano, Evan Granite, International Journal of Coal Geology, 195, 125-138, 2018.

References



9. Analysis of Rare Earth Elements in Coal Fly Ash Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Scanning Electron Microscopy, Robert L. Thompson, Tracy Bank, Scott Montross, Elliot Roth, Bret Howard, Circe Verba, and Evan Granite, Spectrochimica Acta Part B, 143, 1-11, 2018.

10. "Enrichment of Rare Earth Elements from Coal and Coal By-Products by Physical Separations", Ronghong Lin, Tracy Bank, Bret Howard, Yee Soong, Elliot Roth, Evan Granite, Fuel, 200, 506-520, 2017.

11. "Rare Earth Elements in Alberta Oil Sand Process Streams", Elliot Roth, Tracy Bank, Bret Howard, Evan Granite, Energy & Fuels, 31, 4714-4720, 2017.

12. "Organic and Inorganic Association of Rare Earth Elements in Coal", Ronghong Lin, Tracy Bank, Elliot Roth, Yee Soong, Evan Granite, International Journal of Coal Geology, volume 179, 295-301, 2017.

13. "The Future of Rare Earth Elements May Lie with Coal", Mary Anne Alvin, Evan Granite, Charles Miller, American Coal, Issue 2, 28-32, 2017.

14. Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion By-Products, James Hower, Evan Granite, David Mayfield, Ari Lewis, Robert Finkelman, Minerals, 6, 32, 2016.

15. "Analysis of Rare Earth Elements in Geologic Samples using Inductively Coupled Plasma Mass Spectrometry", Tracy Bank, Elliot Roth, Phillip Tinker, and Evan Granite, US DOE Topical Report DOE/NETL-2016/1794, April 14, 2016

16. Characterization and Recovery of Rare Earths from Coal and By-Products, Evan J. Granite, Elliot Roth, Mary Anne Alvin, EM, June 2016.

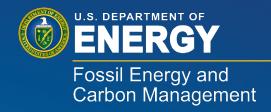
17. "Recovery of Rare Earths from Coal and By-Products - A Paradigm Shift for Coal Research", Evan J. Granite, Elliot Roth, Mary Anne Alvin, National Academy of Engineering's The Bridge, 46(3), 56-57, Fall 2016.

18. Resolution of BaO Interferences on Eu Peaks in Fossil Energy Byproduct Samples Using High-Resolution Sector-Field ICP-MS, Robert L. Thompson, Tracy Bank, Elliot Roth, and Evan Granite, Fuel, vol. 185, 94-101, December 2016.

Disclaimer

This paper/information was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.



Beyond Combustion – Coal in the 21st Century

Evan Granite Alaska Core-CM Stakeholders Meeting

September 2023



Carbons from Coal



Numerous Possibilities

- Activated Carbons
- Coke
- Chars
- Graphite and Carbon Electrodes
- Graphene
- Nanocarbons
- Composites and Alloys
- Carbon Fibers, Blocks, Roof Shingles, Deck Boards, Pipes
- Carborundum (Silicon Carbide), Diamond



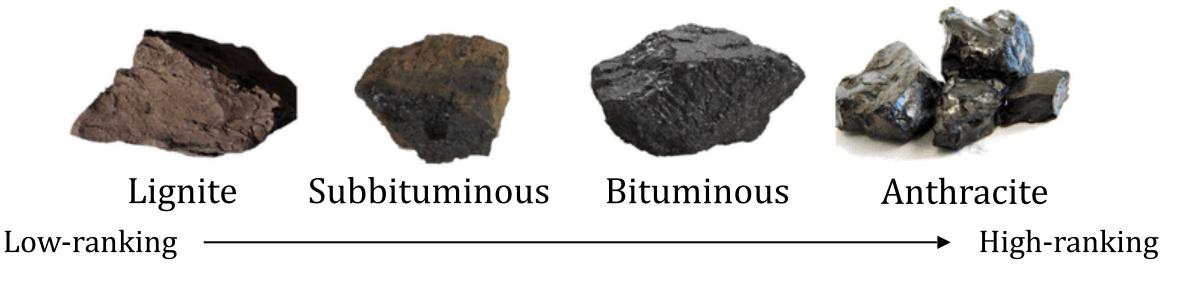
Program Overview

- Current and Recent Projects (41) Covering Building Materials (Bricks, Blocks, Deck Boards, Roof Shingles), Silicon Carbide, Beneficiation, Graphite, Carbon Fibers, Nanomaterials, Activated Carbons, Composites
- Completion of Current Projects
- Focus on Clean Energy High Value Materials
- High Volume Materials
- Graphite is a Critical Material
- Use of Byproduct Carbons from Critical Material Recovery
- Many Synergies with Critical Materials Program

Motivation for the Program

- Develop Clean Energy & Novel High Value Carbon Products to Incentivize and Facilitate Clean-Up of Waste Coal and Coal Byproduct Impoundments
- Use of Byproduct Carbons from Critical Material Recovery
- Focus on Clean Energy & Highest Value Products Such as Graphene, Nanocarbons, Graphite, Battery Electrodes, Specialty High Surface Area Activated Carbons, Novel Alloys, Fibers
- Develop High Volume Products Such as Building Materials
- Bricks, Blocks, Roof Shingles, Pipes, Deck Boards

What is Coal? **Palette with Many Possibilities**



Classic Analysis – Moisture, Volatile Matter, Fixed Carbon, Ash Sequentially Dry, Pyrolyze and Burn Coal Weight Loss From Each Step Yields – Moisture, VM, FC, and Ash (balance)



Coal Classifications



Class and group	Fixed carbon, %	Volatile matter, %	Heating value, Btu/lb	
I. Anthracitic				
1. Metaanthracite	>98	<2	9 C	
2. Anthracite	92-98	2-8		
3. Semianthracite	86-92	8-14		
II. Bituminous				
1. Low volatile	78-86	14-22		
2. Medium volatile	69-78	22-31		
3. High volatile A	<69	<31	>14,000	
4. High volatile B			13,000-14,000	
5. High volatile C			10,500-13,000	
III. Subbituminous				
1. Subbituminous A			10,500-11,500	
2. Subbituminous B			9,500-10,500	
3. Subbituminous C			8,300-9,500	
IV. Lignitic			i presente de la companya de la comp Del companya de la comp	
1. Lignite A			6,300-8,300	
2. Lignite B			<6,300	

ASTM Coal Classification by Rank (2)



Graphitization in Nature – Coal and Graphite



Table 2. Variations of Physical and Chemical Properties with Rank and Their Useful Range as Rank Parameters c

Classification	% C (daf) ^a of Vitrinite	Vol. Matter % daf ^a	Moisture % in Situ	Cal. Value BTU/LB (af) ^b	Reflectance % (Vitrinite)	Important Characteristics	Applicability of Propertie as a Rank Parameter	
Peat	60					1. Free Cellulose 2. Plant Detail Recognizable		
Soft Brown Coal						1. No Frée Cellulose 2. Plant Structure Recognizable	n Situ	
Lignite		53	35	7,200	~0.3		(af) ^b Moisture in Situ	
	~71	49	25	9,900		1. Plant Structure Still Partly Recognizable	Mois	
Subbituminous	77	42	8-10 -	12,600	~0.5	2. Vitrinite Formed	alue /alue	
High Volatile Bituminous	87	29	- 8-10 -	12,600 -		Low-Reflecting Exinite	ce of Vitrinite Calorific Value (af) ^b % Moist	
Med Vol. Bit. Low Vol. Bit. Semi-Anthracite	- 67	23		15,500	1.1	Exinite Lighter in color Exinite Vitrinite	Aeflectance	
Semi-Anthracite	0.1			15 000	2.5	Indistinguishable	Matte	
Anthracite Meta Anthracite	91	8		15,000	2.5	Anisotropic Reflectance	% C daf, ^a P Volatile Mat X-Ray Diffraction % H daf ^a	
Graphite	100	0	•					

a daf-Dry Ash Free

^b af—Ash Free

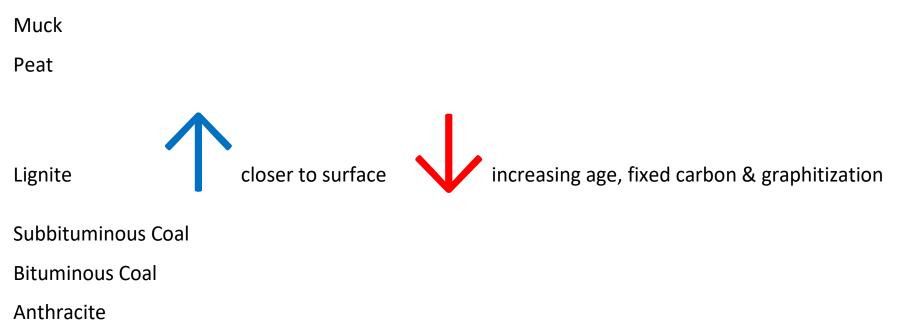
^c Adapted from: "Coal and Coal Bearing Strata," (*Editors:* D. Murchison and T. S. Westall), and "The International Handbook of Coal Petrography," International Committee for Coal Petrology



Graphitization in Nature – Coal and Graphite



 Table 1.
 Coal and Coal-Related Carbonaceous Materials in Nature (from Schobert 1989)





Graphitization in Nature – Coal and Graphite



Graphite Formed in Nature

- Elevated Temperatures/Pressures
- Or Contact with Hot Magmatic Fluids
- Typically, Over Eons ("Coalification/Graphitization")
- Muck Peat Lignite Subbituminous Bituminous Anthracite Meta Anthracite – Graphite
- "The Geochemistry of Coal Part I. The Classification and Origin of Coal", Harold H. Schobert, Journal of Chemical Education, 242-244, 1989.
- "The Geochemistry of Coal Part II. The Components of Coal", Harold H. Schobert, Journal of Chemical Education, 290-293, 1989.



Abundant Domestic Coal – Largest World Reserves Abundant Coal Reserves in the U.S.



Source: Fletcher & Baylis/Science Source

Estimated Recoverable Reserves

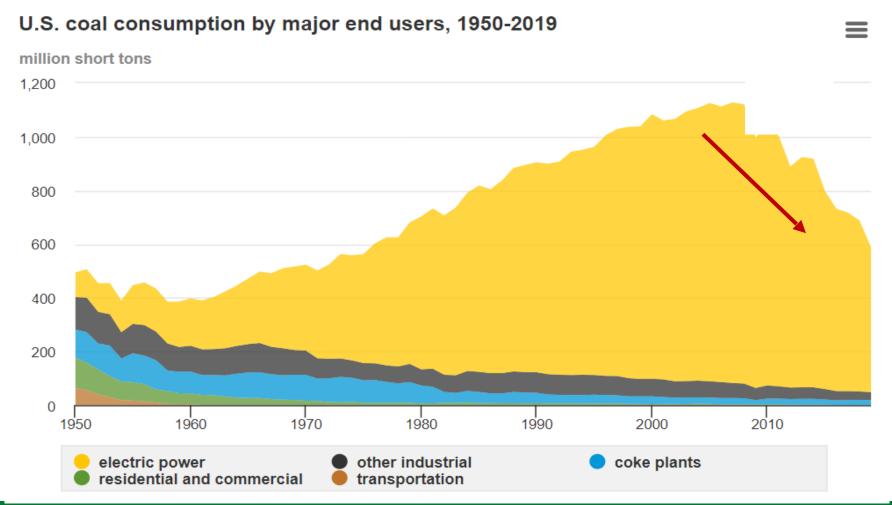
- Coal that can *currently* be mined
- 253 billion short tons

Demonstrated Reserve Base

- Total amount of coal that could *feasibly* be mined
- 474 billion short tons



Declining Domestic Production and Consumption Trends in U.S. Coal Consumption





Source: U.S. Energy Information Administration, *Monthly Energy Review*, Table 6.2, May 2020

Declining US Coal Production



Coal and Waste Coal – Resource

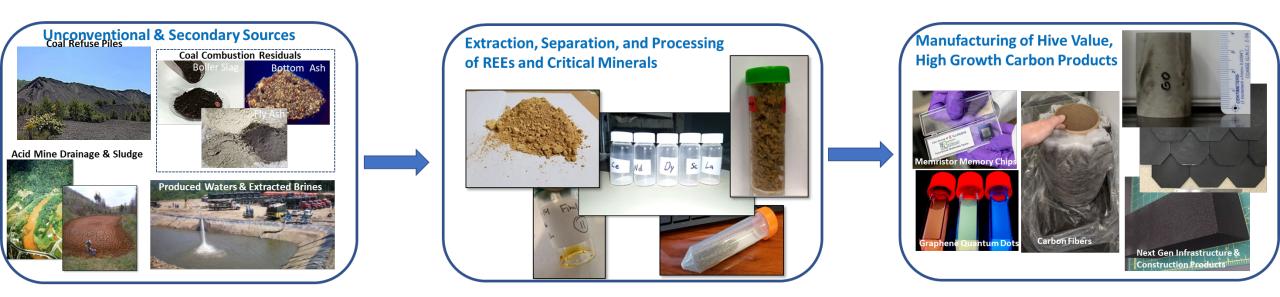
- US Has 250 300 Year Supply Coal
- Largest in the World by a Wide Margin
- Approximately 1 1.1 billion tons/year Produced from 1990 2014 (EIA)
- 535 Million Tons in 2020; 578 Million Tons in 2021 (EIA)
- US Coal Most Used for Generation Electricity
- Retirements of Older Coal-Burning Power Plants
- Inexpensive Natural Gas
- Activated Carbons, Chemicals, Tars, Steel, Exports
- We Can Do So Much More with Coal, Waste Coal and Byproducts



Principles of Waste Minimization and Circularity

Reclaiming, recycling waste materials

Maximizing use of feedstock materials







Two Typical Routes

1. Combustion

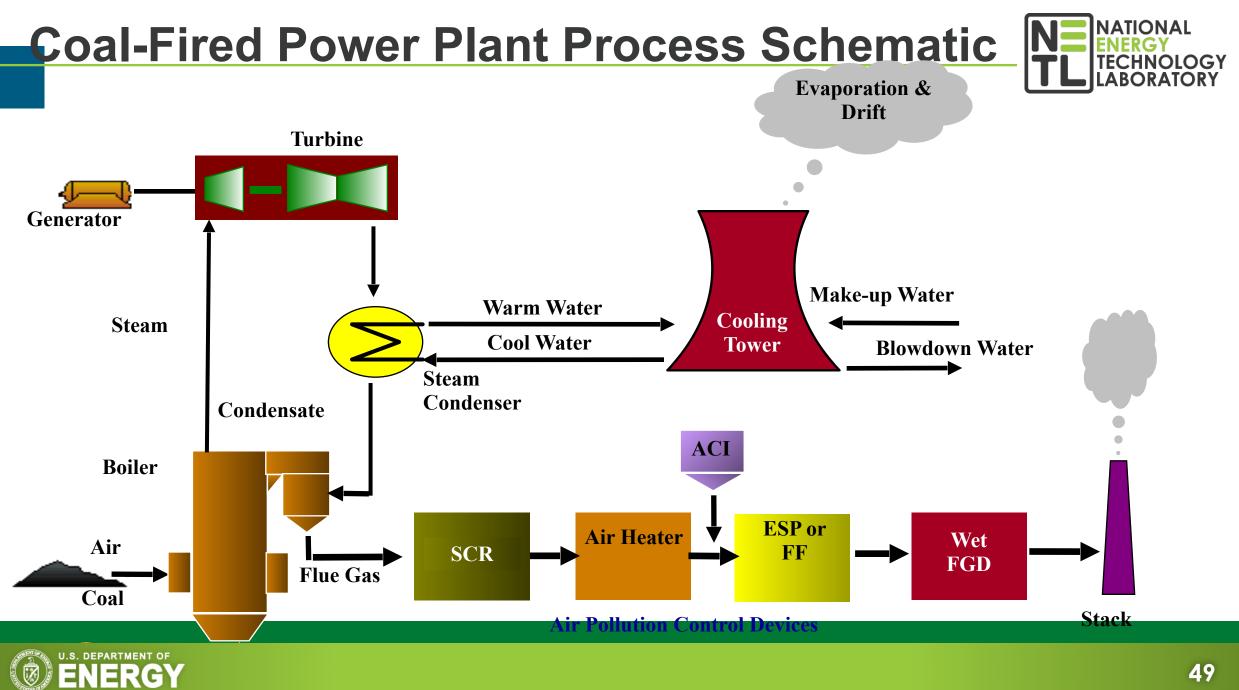
Power Generation, Heat

• 2. Pyrolysis and Gasification

Chemicals, Tars, Liquid Fuels, Activated Carbons, Power Generation

Under Carbon Ore – Novel Carbons, Typically by Pyrolysis





Gasification



• Carbon – Steam or Carbon – Carbon Dioxide Reactions

 $C + CO_2 \rightarrow 2 CO$

- $C + H_2O \rightarrow CO + H_2$
- To make Syngas (Fuel Gas)
- Primarily CO and H₂
- Burn to Make Electricity
- Convert to Chemicals and Fuels
- FT Process
- Methanol, Synthetic Gasoline, Waxes,.....



What is Gasification & Fuel Gas (Syngas)?

- Carbon-Steam Reaction
- Pyrolysis "Thermally Neutral" ΔH Small
- Combustion
- Elevated Pressure

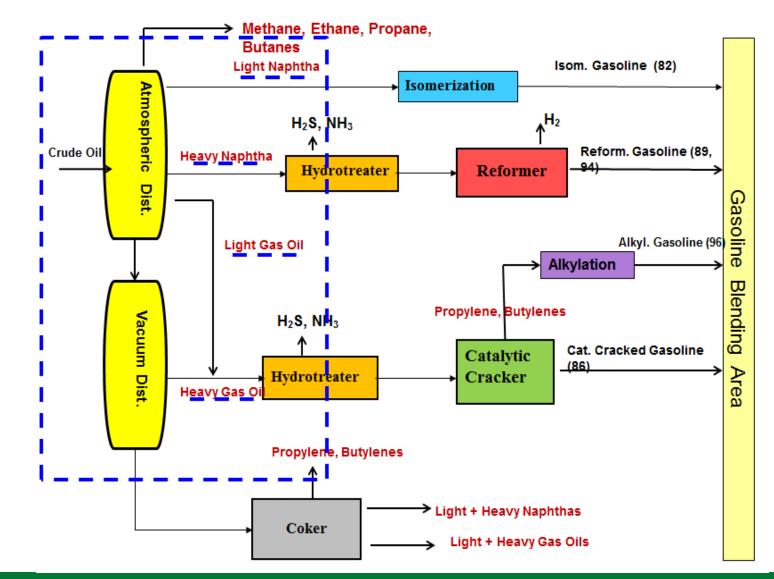
Major Products

• CO, H₂, CO₂, H₂O, Tars & HCs, Chars

Minor Products

- \bullet $\rm NH_3$, HCl, $\rm Cl_2$ and particulates
- H₂S, COS, CS₂
- Trace Contaminants: Hg, AsH₃, H₂Se, and PH₃

Petroleum Refinery – Uses Every Part of the Fossil Fuel





ORNL Projects FWP-FEAA155 – C4AWAR

- "Coal Conversion for Carbon Fibers and Composites"
- 10 MM Graphite, Fibers, and Composites Lab-Scale R&D

FWP-FEAA157

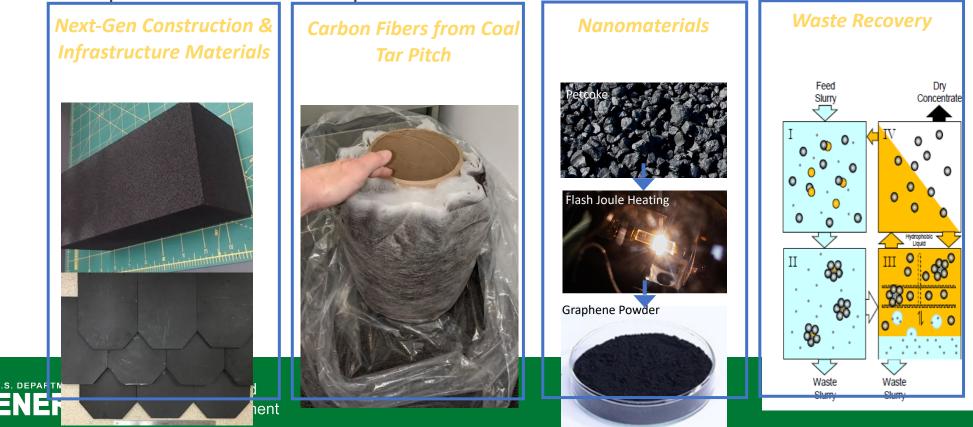
- "Scale-up Production of Graphite and Carbon Fibers from Coal and Coal Refuse"
- 10 MM Scale-Up at Oak Ridge Carbon Fiber Pilot Facility
- Carbon Fibers Envisioned for Lightweight Automobiles
- Graphite for Batteries (New ORNL Technology for Graphite)

Carbon Ore to Products: Opportunities Toward a Clean Energy Transition



Advanced processing of carbon ore and associated by-products for the development of everyday and high value carbon products

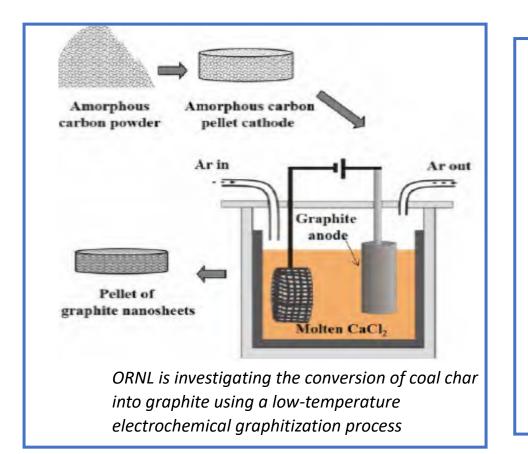
- Generated predominantly from *coal waste and refuse* toward remediation
- Enable domestic manufacturing of strategic materials to encourage job creation
- Ensure the health and safety of the environment and people around the use and disposal of carbon-based products

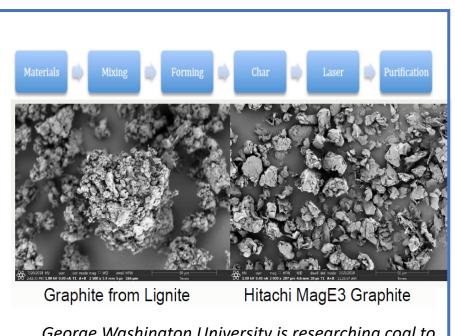


Transformation of Carbon Ore to Graphite



To address anticipated increase in demand, funding research on synthetic graphite





George Washington University is researching coal to Li-ion battery grade (potato) graphite

FOA 2405: "Advanced Coal Waste Processing



Carbon Electronics: Memristor Computer Memory









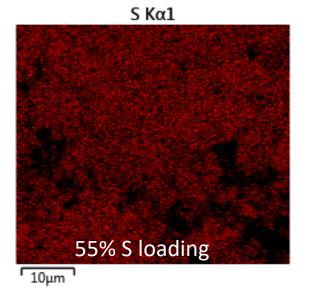
- Memristor computer memory devices:
 - Emerging memory technology
 - Energy efficient (<pJ/operation)
 - High speed (10 ns)
 - Easily miniaturized (10 X 10 nm)
 - Integrable on logic chip
- Coal carbons outperform other carbons and metal oxides:
 - Lower cost fabrication method
 - Improved device-to-device reproducibility
 - Better long-term device stability

Coal Materials: Engineered Graphene Quantum Dots

Porous carbons for energy storage, chemical rocessing, & filtration applications

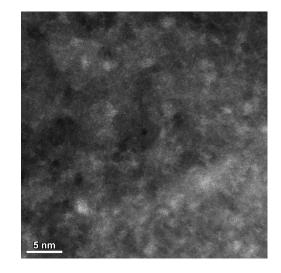


Energy Storage



- Application: LiS battery
- 25-33% increase in S loading w.r.t. SOTA

Chemical Processing



- Applications: CO₂ Utilization, Chemical processing, synthetic fuels
- Single metal atoms dispersed on carbon
- Unprecedented activity for , H₂ , O₂ , CO, CO₂, organic decomp

Filtration & Membranes



NIL

Massachusetts Institute of Technology

- Ideal pore size for water desalination, testing in progress at NETL
- Solid carbon membranes w/ MIT



Coal Materials: Porous Carbons, Nanoporous Membranes

Current Portfolio – Pyrolysis of Coal Waste Minimization

- Pyrolysis Heat Coal in Absence of Air
- Outstanding Strategy for Upgrading Coal
- Thermally Neutral : ΔH_{Reaction Pyrolysis} is Small
- Decomposition of Volatile Matter & Graphitization of Carbon
- Produce Char, Tar and Gases
- Focused Upon Char or the Tar (For Carbon or Pitch)
- Results in Wasted Gas, Tar and/or Char
- Future Work Utilize All of The Pyrolysis Products
- No Wasted Molecules

X-MAT – Tour April 7, 2022





energy.gov/fe

X-MAT – Tour April 7, 2022





energy.gov/fe

FOA 2620

- Released July/August 2022
- AO1: Graphite (Synergy with Critical Materials)
- AO2: Composites and Novel Alloys
- 6 MM Total
- Selections Announced
- <u>https://www.energy.gov/fecm/articles/doe-invests-6-million-</u> <u>develop-useful-products-coal-and-coal-wastes-support-clean</u>
- DOE Invests \$6 Million to Develop Useful Products from Coal and Coal Wastes in Support of a Clean Energy Economy
- February 16, 2023

Future Research

a) High Value Products for Clean Energy Economy - Carbon Nanomaterials, Graphite, Specialty Ultra-High Surface Area Activated Carbons, Fibers, Composites, Novel Alloys, Diamonds

- b) Utilization of Entire Coal Value Chain Volatile Matter (Tars and Pitch – Fibers; Gases - Chemicals), Mineral Matter (Critical Minerals), Fixed Carbon (Carbon Nanomaterials, Graphite, UHSAAC) – No Wasted Molecules – Multiple Products -Better Process Economics – Greater Incentive to Clean-Up Coal Impoundments
 - Utilize Byproduct Carbons from Recovery of CMs

• c) Tracking and Removal of Harmful Trace and Minor Element Species – Zero Emissions



In the News https://www.netl.doe.gov/node/12705

 A technology, developed by XMAT with support from DOE, uses coal waste as an anode material in lithium-ion batteries.

<u>https://www.energy.gov/fecm/articles/doe-announces-6-million-develop-useful-products-coal-and-coal-wastes</u>

• FOA 2620

Annual Review Meeting

- Downtown Pittsburgh
- In Person
- October 2022
- Over 40 Presentations on Carbon Ore Research
- Presentations are Available On-line
- <u>https://netl.doe.gov/22RS-proceedings</u>
- Next Program Review
- April 2 4, 2024
- Pittsburgh

Acknowledgements

Brent Sheets

- Arctic Energy Office (Givey Kochanowski, Michael McEleney, Erin Whitney, Carolyn Hinkley)
- FECM Julia Pizzutti, Gabe Hernandez, Brad Crabtree
- Joe Stoffa
- Grant Bromhal
- Kavita Vaidyanathan
- Anna Wendt
- Jennifer Wilcox
- Sarah Forbes
- Mary Anne Alvin
- Savannah Rice
- Acqueetta Ragland-Higdon



Additional Information

- Much additional information is available on the NETL Carbon Ore website:
- <u>https://netl.doe.gov/Carbon-Ore-Processing</u>
- A factsheet is also available:
- <u>https://netl.doe.gov/sites/default/files/2022-11/Program-151_0.pdf</u>



Fossil Energy and Carbon Management

Questions evan.granite@hg.doe.gov joseph.stoffa@netl.doe.gov



Disclaimer

This paper/information was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Permission was granted by X-MAT for use of photos.