

## **Beyond Combustion – Coal in the 21<sup>st</sup> Century**

#### Evan J. Granite Resource Sustainability Review Meeting April 2, 2024





#### Numerous Possibilities

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



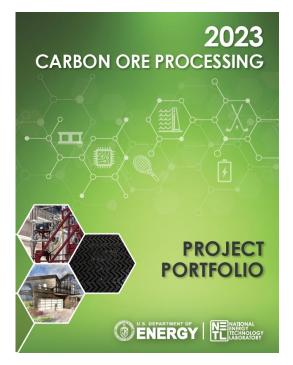
## **Program Overview**

- Current and Recent Projects (49) 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



## **DOE Carbon Ore Portfolio**

- 23 active in 2024 and 2025
- https://netl.doe.gov/node/2476?list=Carbon%20Ore%20Processing
- Graphite
- Nanocarbons
- Supercapacitors
- Activated Carbons
- Silicon Carbide
- Building Materials
- Composites
- Moving Towards High Value Products

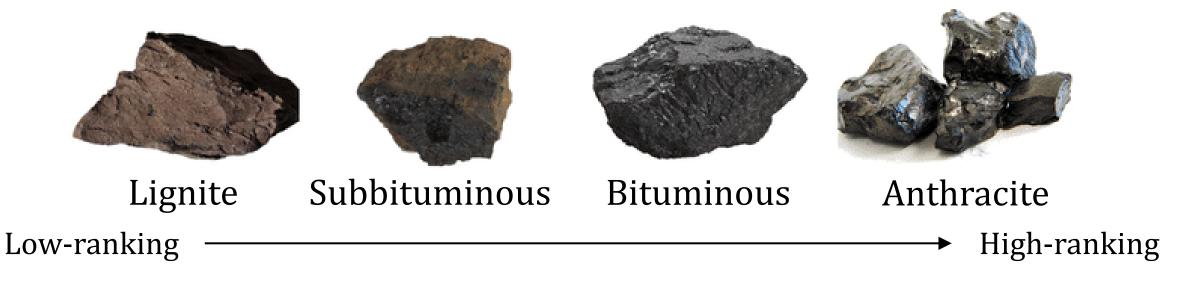




## **Motivation for the Program**

- 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		
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			a de la deservición de la construction de l	
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) <sup>a</sup> of Vitrinite	Vol. Matter % daf <sup>a</sup>	Moisture % in Situ	Cal. Value BTU/LB (af) <sup>b</sup>	Reflectance % (Vitrinite)	Important Characteristics	Applicability of Propertie as a Rank Parameter
Peat	60	2	75			1. Free Cellulose 2. Plant Detail Recognizable	
Soft Brown Coal	00					1. No Free Cellulose 2. Plant Structure Recognizable	in Situ
Lignite	~71	53 — 49 —	35	9,900	~0.3	1. Plant Structure Still	ture
Subbituminous	77	49	8-10 -	12,600	~0.5	Partly Recognizable 2. Vitrinite Formed	/alue //alue
High Volatile Bituminous	87	29	- 8-10 -	12,600		Low-Reflecting Exinite	ce of Vitrinite Calorific Value (af) <sup>b</sup>
Med Vol. Bit. Low Vol. Bit. Semi-Anthracite		20		15,500	1.1	Exinite Lighter in color Exinite Vitrinite	ter daf <sup>a</sup>
Anthracite	91	8			2.5	Indistinguishable Anisotropic	C daf, <sup>a</sup> latile Ma Ray Fraction H daf <sup>a</sup>
Meta Anthracite Graphite	100	o	-			Reflectance	S S S S

a daf-Dry Ash Free

<sup>b</sup> af—Ash Free

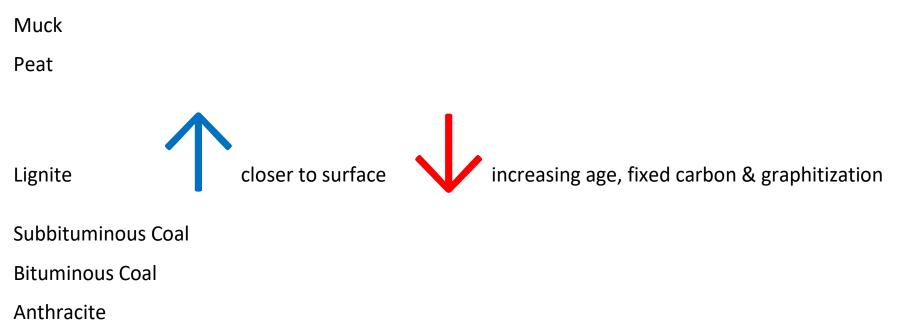
<sup>c</sup> Adapted from: "Coal and Coal Bearing Strata," (*Editors:* D. Murchison and T. S. Westall), and "The International Handbook of Coal Petrography," International Committee for Coal Petrology



## **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**

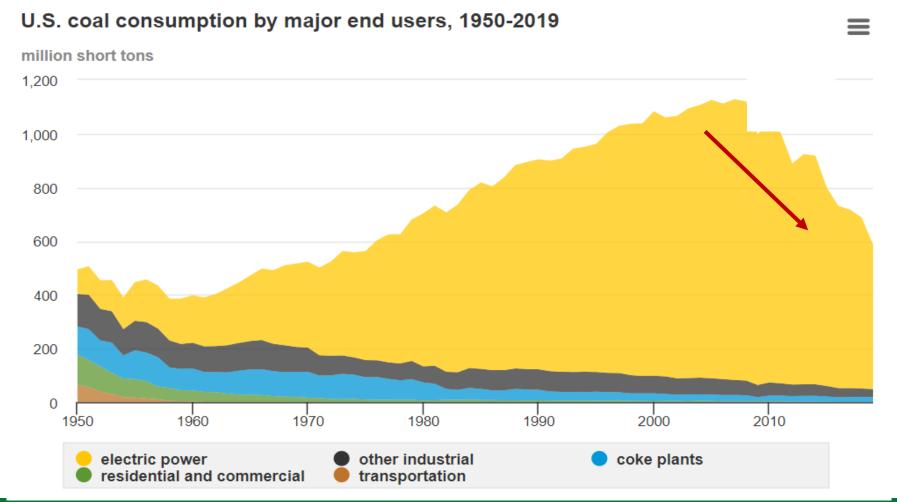
- Coal that can *currently* be mined
- 253 billion short tons

#### **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)
- 577 Million Tons in 2021; 594 Million Tons in 2022 (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

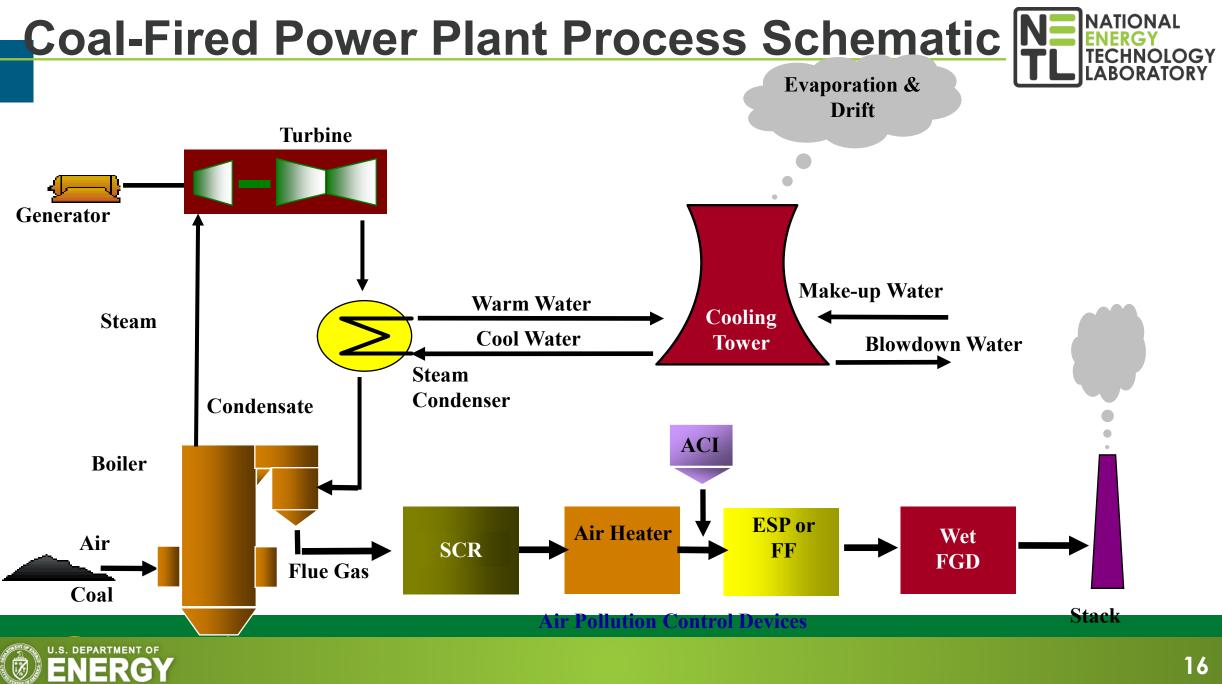
**Power Generation, Heat** 

## 2. Pyrolysis and Gasification

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

## **Under Carbon Ore – Novel Carbons, Typically by Pyrolysis**





#### **Gasification**

- **NETIONAL** ENERGY TECHNOLOGY LABORATORY
- 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 H<sub>2</sub>
- 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"  $\Delta H$  Small
- Combustion
- Elevated Pressure

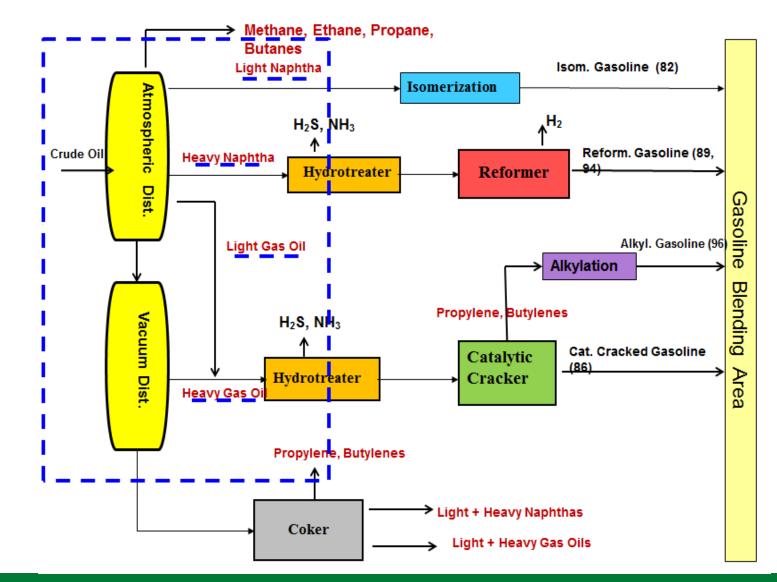
## **Major Products**

• CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, Tars & HCs, Chars

## **Minor Products**

- NH<sub>3</sub>, HCl, Cl<sub>2</sub> and particulates
- H<sub>2</sub>S, COS, CS<sub>2</sub>
- Trace Contaminants: Hg, AsH<sub>3</sub>, H<sub>2</sub>Se, and PH<sub>3</sub>

#### **Petroleum Refinery – Uses Every Part of the Fossil Fuel**





## ORNL and University of Kentucky Projects <u>FWP-FEAA155 – C4AWAR</u>

- "Coal Conversion for Carbon Fibers and Composites"
- Graphite, Fibers, and Composites

### FWP-FEAA157

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

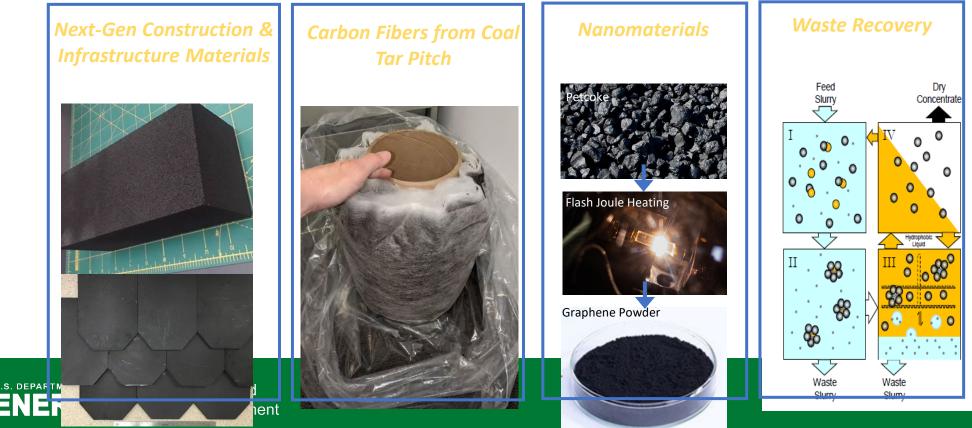


#### Carbon Ore to Products: Opportunities Toward a Clean Energy Transition



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

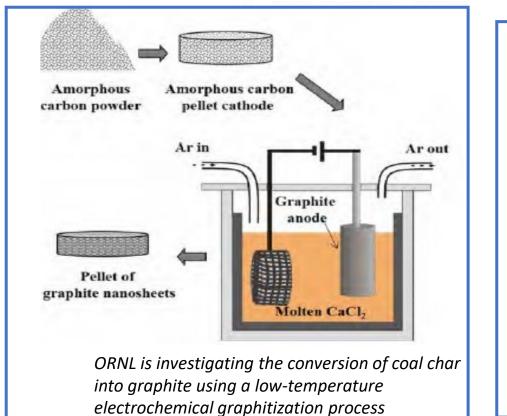
- Generated predominantly from *coal waste and refuse* toward remediation
- Enable domestic manufacturing of strategic materials to encourage job creation
- Ensure the health and safety of the environment and people around the use and disposal of carbon-based products

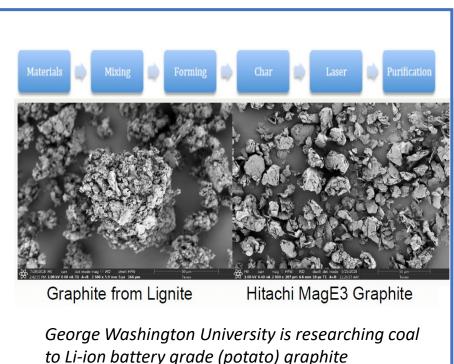


#### **Transformation of Carbon Ore to Graphite**



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



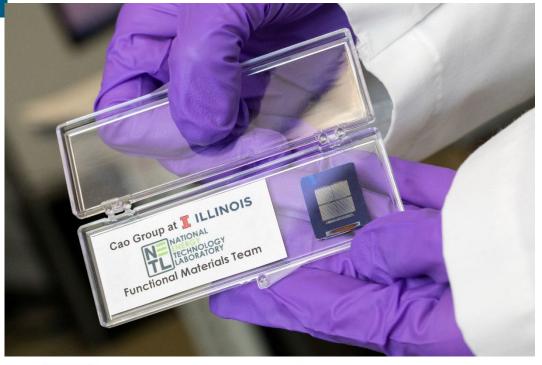


#### FOA 2405: "Advanced Coal Waste Processing



#### **Carbon Electronics: Memristor Computer Memory**









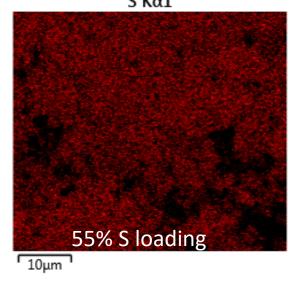
- Memristor computer memory devices:
  - Emerging memory technology
  - Energy efficient (<pJ/operation)</li>
  - High speed (10 ns)
  - Easily miniaturized (10 X 10 nm)
  - Integrable on logic chip
- Coal carbons outperform other carbons and metal oxides:
  - Lower cost fabrication method
  - Improved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

#### **Coal Materials: Engineered Graphene Quantum Dots**

# Porous carbons for energy storage, chemical processing, & filtration applications

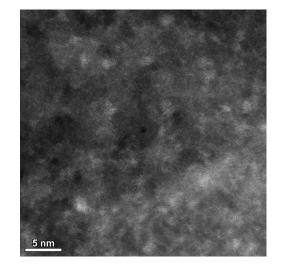


## Energy Storage



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

#### **Chemical Processing**



- Applications: CO<sub>2</sub> Utilization, Chemical processing, synthetic fuels
- Single metal atoms dispersed on carbon
- Unprecedented activity for , H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, organic decomp

### **Filtration & Membranes**



- 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<sub>Reaction Pyrolysis</sub> 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 Meetings**

- Downtown Pittsburgh
- October 2022
- Over 40 Presentations on Carbon Ore Research
- Presentations are Available On-line
- https://netl.doe.gov/22RS-proceedings
- Today's Program Review
- April 2 4, 2024
- Pittsburgh
- <u>https://netl.doe.gov/events/24RS</u>

### Acknowledgements

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- Brent Sheets
- Arctic Energy Office (Givey Kochanowski, Michael McEleney, Erin Whitney, Carolyn Hinkley)
- FECM Julia Pizzutti, Gabe Hernandez, Brad Crabtree

## **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:
- https://netl.doe.gov/sites/default/files/2022-11/Program-151 0.pdf



## **Graphite and Carbon Electrodes**



energy.gov/fe



- Critical Mineral (USGS) and a Critical Energy Material (USDOE) **Natural Graphite**
- US Imported 84,000 Metric Tons in 2023
- **100% Import Reliance**
- Import Sources: (2019-2022) China 42%; Mexico, 16%; Canada, 15%; Madagascar, 12%; other, 15%.
- The major uses of natural graphite were batteries, brake linings, lubricants, powdered metals, refractory applications, and steelmaking.
- The number of lithium-ion battery manufacturing facilities in the United States increased to 10 in 2023 from 3 in operation during 2019.
- An additional 28 facilities were under development.
- U.S. Geological Survey, 2024, Mineral commodity summaries 2024: U.S. Geological Survey, 212 p., https://doi.org/10.3133/mcs2024.

## **Domestic Demand for Graphite Will Grow**



- "Very crude back of the envelope estimates for US EV market" the current domestic annual automobile/SUV demand is around 15.5 million cars/year (2023).
   The DOE has a goal of 50% EV adoption by 2030. Assuming this DOE goal is met,
- EV car batteries contain approximately 150 lbs. of graphite. Assuming 3% annual increase in annual automobile demand (23% increase in automobile demand for 2030, 19 million cars/year in 2030):
- 19,000,000 cars sold in 2030/year \* 0.5 EV \* 150 lbs. graphite/electric vehicle \* 1 ton/2,000 lb. = 713,000 tons graphite required for 2030 US EV demand
- Versus 92,000 tons (84,000 metric tons) in 2023
- Not accounting for Electric Trucks, Consumer Batteries,.....

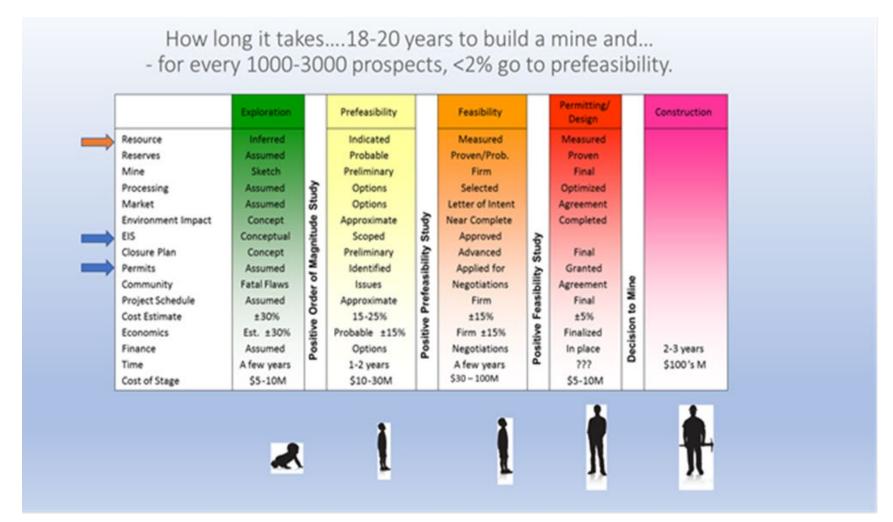
## What Can We Do to Meet Burgeoning Demand?



- New Domestic Mines (Alabama, Alaska, Montana)
- New Domestic Processing Facilities (Cleaning the Natural Graphite)
- This Takes Time
- On Order of 10 20 Years
- Resource Characterization Extensive Sampling Program to Quantify
- Engineering Designs Mining and Processing of Ore
- Financing Many Millions of Dollars
- Permits For Both Mining and Processing of Ore
- Construction and Shakedown

## **Typical Mine Project Timeline**







• Figure is courtesy of Lance Miller, Vice President, Natural Resources, NANA, from his presentation "Alaska Critical Mineral Resources", DOE-DOD Seminar Series on Critical Materials, February 8, 2024.



### **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
  - → Similar to Acheson Process Albeit Much Slower!



## **Synthetic Graphite**



- Produced by Heating Carbonaceous Materials to 3,000 4,000°C
- For Long Periods of Time
- Acheson Process 1890
- Others (Petroleum Coke)
- Energy Intensive
- Polluting
- DOE is Seeking Alternative (Lower Temperature) Methods

Value-Added Products from Coal



Part 1. Graphite (and Carborandum)

- Multi-Billion Dollar Annual Industry
- Various Precursors
- Thermal Formation
- Edward Acheson 1890
- Making Silicon Carbide by Heating Coke and Sand to 3000°C
- Form Graphite at Even Higher Temperatures (4000°C)
- By Thermal Decomposition of Silicon Carbide
- Carbon + Sand  $\rightarrow$  Silicon Carbide (Carborandum SiC)  $\rightarrow$  Graphite
- Anthracite an Optimum Feed for His Process



## Edward Acheson (1856-1931)



- Prolific Inventor (70 Patents)
- Western Pennsylvania
- Worked for Edison
- Interested in Making Diamonds
- Industrial Abrasive
- Through Heating Carbon at High Temperatures
- Ended Up Making Silicon Carbide
- And Graphite
- Processes Used to this Day



**Catalysts for Thermal Graphitization** 

Abundant Literature



- Review Rongyan Wang, "Catalytic Graphitization of Coal-Based Carbon Materials with Light Rare Earth Elements", Langmuir 2016, 32, 8583–8592
- La, Ce, Pr, Fe, Co, Ni, Si (Acheson), Ti, W, Mo, Cr
- Still Require High (Typically 2700°C) Temperatures
- One of the Best  $CeO_2 CaCO_3$  or  $MnO_2$  US Patent 3,615,209
- 2200°C 88 100% Graphitization
- Fe catalysts 1300°C
- "Fe based catalysts for petroleum coke graphitization for Lithium Ion battery application", Agung Nugroho, Materials Letters, 303, 130557, 2021
- Mechanisms: Carbide Formation (Acheson), Orientation, Nucleation



# Low Temperature Production of Graphite



Graphite can be synthesized from either coal or petroleum coke at high temperatures of 3000 – 4000 °C. These high temperatures make the production of synthetic graphite an expensive and environmentally damaging endeavor. The United States has over four billion tons of waste coals, scattered in over one thousand impoundments.

The DOE is investigating concepts for production of graphite from abundant waste coals, at temperatures below 1800°C. This would facilitate clean-up of the waste coal sites and spur production of domestic graphite in a more environmentally friendly and economical manner.

### **Key Challenges in the Technology Area**

- The impact of impurities in the waste coals on the formation of the graphite product.
- Disposition and mitigation of release of toxic elements within the coal such as mercury, arsenic, selenium, cadmium, phosphorus, antimony, sulfur, nitrogen, and halogens.
- Disposition of uranium and thorium present in the feed coal
- Mitigation of organic pollutants
- Economics of the lower temperature processes versus the commercial processes for production of graphite
- Verification of the final synthetic graphite product being highly suitable for use in batteries.
- Producing a brief techno-economic analysis showing creation of a significant number of stable domestic jobs.
- Demonstration of enhancing environmental justice for communities negatively impacted by the waste sites.

## **Recent Technical Accomplishments – Carbon Ore**



### **Low Temperature Production of Graphite**

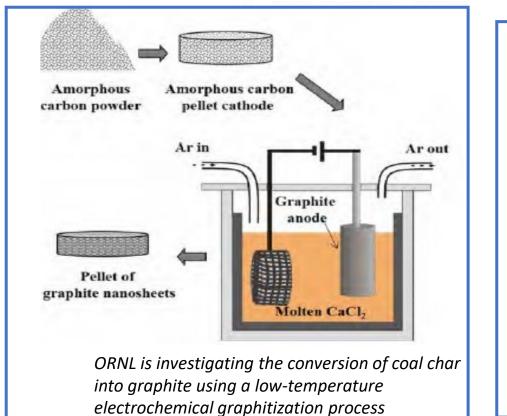
Graphite can be synthesized from either coal or petroleum coke at very high temperatures of 3000 – 4000°C. These high temperatures make the production of synthetic graphite an expensive and environmentally damaging endeavor. NETL showed iron is an effective catalyst for converting coal to graphite at much lower temperatures of around 1500°C. Additionally, both the catalyst & acid used to recover it can be recycled and reused to produce graphite that performs well in lithium-ion battery tests. This effort has significance for utilizing abundant domestic waste coals for fabricating battery anodes, at largehttps://www.netl.doe.gov/node/12897 September 19, 2023, NETL website scales.

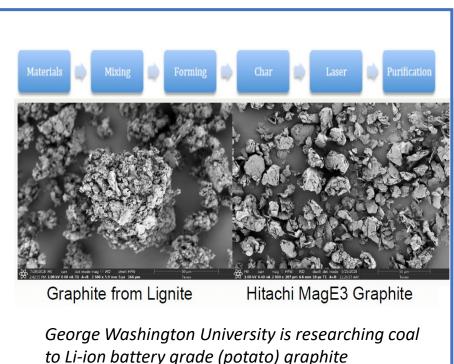
- Other Significant Breakthroughs by George Washington University and ORNL
- Laser Method, Electrochemical Cell

## **Transformation of Carbon Ore to Graphite**



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





#### FOA 2405: "Advanced Coal Waste Processing





**New Battery Electrodes** 

- Carbon, but not Graphite
- Such as Carbon Silicon Materials
- Adoption of Non-Graphite Carbons Would Disrupt Projections for Graphite Demand
- DOE Research

## **SBIR Topic**



### **Direct Use of Coal or Carbonaceous Coal Wastes as Lithium-Ion Battery Anodes**

- Potential SBIR Topic
- Maximum Phase I Award Amount: \$250,000
- Maximum Phase II Award Amount: \$1,600,000
- Less Expensive Alternative to Graphite
- 50% Coal or Waste Coal Content
- May Use Silicon or Other Materials
- Projected Explosive Demand for Carbon Electrodes in Lithium Batteries
- FY24-Phase-I-Release-2-TopicsV612082023.pdf (osti.gov)
- Posted January 18, 2024; Applications Due in March 2024; Awards in June
- Accepting SBIR Phase I Applications: YES
- Accepting STTR Phase I Applications: YES



## Coal-Derived Battery Anodes Show Great Commercial Promise <u>https://netl.doe.gov/node/12705</u> July 19, 2023, NETL website news item

DOE supported R&D of Semplastics' technology to utilize domestic, abundant, and inexpensive coal-derived lithium-ion battery anodes as an alternative to graphite. This technology received the Voltage Award from the Battery Innovation Center, which recognizes an emerging company and/or technology with the highest potential to make a difference in batteries and electrification. Under this agreement, coal-derived lithium-ion battery anodes have been tested extensively in 18650 cells, an industry standard size used in BEVs such as the Tesla Model S & X.



### **New Battery Chemistries and Materials**

- Nearly Infinite Number of Possibilities/Combinations
- EMF Series Thermodynamics of Oxidation/Reduction Suggests Possible Electrodes
- Electrolytes Aqueous, Solid, Ions,.....
- Issues Energy Density, Lifetime, Charge/Recharge Cycles and Kinetics, Safety, Cost, Material Availability, Fabrication, Geometry, Electrode Morphologies, .....
- Typically Takes Years of Testing to Perfect
- Microsoft and PNNL AI Initiative to Speed Up Battery Development
- <u>https://quantum.microsoft.com/en-us/our-story/quantum-elements-overview</u>
- <u>https://cloudblogs.microsoft.com/quantum/2023/08/09/accelerating-materials-discovery-with-ai-and-azure-quantum-elements/</u>
- Adoption of New Batteries Would Disrupt Future Need for Graphite
- DOE Research

**Conclusions/Future Work** 

- Acheson Process and Recent Variations Great Success
- Carbon + Sand  $\rightarrow$  Silicon Carbide (Carborundum SiC)  $\rightarrow$  Graphite

### **Challenges**

- Energy Intensive (3000-4000°C)
- Slow (Heating in Two Steps: 1000°C, 3000-4000°C)
- Impurities in Coal (and Cokes)

### Future Work (Synthetic Graphite)

- Reduce Required Temperatures, Reaction Times, and Energy
- Produce Other Value-Added Carbons and Products
- Capture and Account for the Pollutants
- Routes: Catalysts, Electrochemical (ORNL), Laser Heating (GWU), Thermal (UKY)

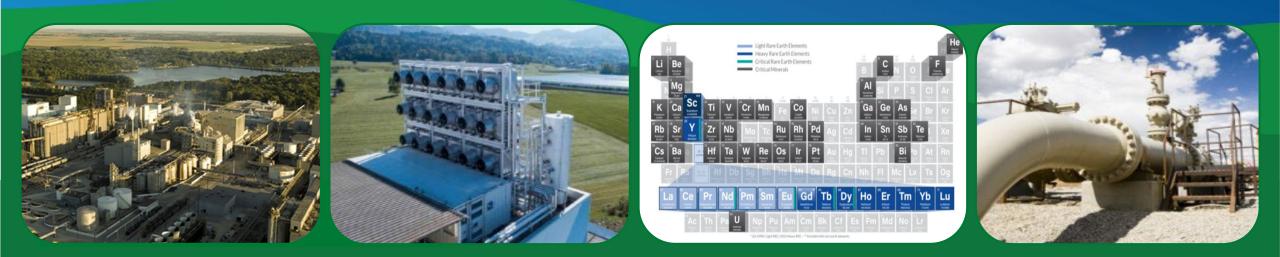






Fossil Energy and Carbon Management

# Questions <u>evan.granite@hq.doe.gov</u> joseph.stoffa@netl.doe.gov



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