DOE Critical Minerals & Materials

Potential Resources From Abundant Domestic Wastes, Byproducts and Non-Traditional Sources

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Introduction: "Dynamic Dozen" Critical Materials

GOALS

● 100% clean electricity by 2035: 30 GW offshore wind by 2030 ●

● Zero-emission transportation: 50% EV adoption by 2030 ●

- Neodymium, Praseodymium and Dysprosium for magnets → Magnets enable efficient electric machines including wind generators, electric and fuel cell vehicle motors, industrial motors
- Lithium, Cobalt, Nickel, Graphite, and Manganese for energy storage → Batteries are needed for electric vehicles and grid storage to enable high penetration of zero-emission transportation and intermittent clean power generation
- Iridium & Platinum for electrolyzers; Platinum for fuel cells → Iridium and platinum for electrolyzers are needed for green hydrogen production and platinum for fuel cells used in transportation and stationary energy storage.
- Gallium for wide bandgap semiconductors, LEDs → Wide bandgap power electronics enable high voltage power generation (like wind) to connect to the grid
- Germanium for microchips (semiconductors) → 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

Characteristics of Wastes and Byproducts of Interest

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- 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

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- 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 – **Heat is our Friend !**
- 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

Heat is Our Friend

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

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• 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)

Estimated Average Concentrations in US Coal Ash

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• 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

Estimated Quantities in US Legacy Coal Ash

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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

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• Nd	172,000 tons	~ 40-year supply (estimate)
• Dy	62,000 tons	~ 14-year supply (estimate)
• Li	288,000 tons	130-year supply
• Co	110,000 tons	15-year supply
• Ni	252,000 tons	1.1-year supply
• Ir	40 tons	15-year supply
• Pt	600 tons	15-year supply
• Ga	20,000 tons	1,100-year supply
• Ge	130,000 tons	3,900-year supply

U.S. Geological Survey, 2022, Mineral Commodity Summaries

Next Steps

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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

Municipal Solid Waste

- 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**
- **https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials**
- **https://archive.epa.gov/epawaste/nonhaz/municipal/web/html/**
- EPA and Literature for Detailed Compositions

Municipal Sewage Sludge

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- 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
- https://www.epa.gov/biosolids/basic-information-about-biosolids
- https://www.epa.gov/biosolids/sewage-sludge-surveys
- https://www.epa.gov/sites/default/files/2021-04/documents/tnsss-appendix-elemental-analyses-report.pdf

- EPA and Literature for Detailed Compositions

Red Mud

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- 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

Steel

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- 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

Smelter Wastes

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

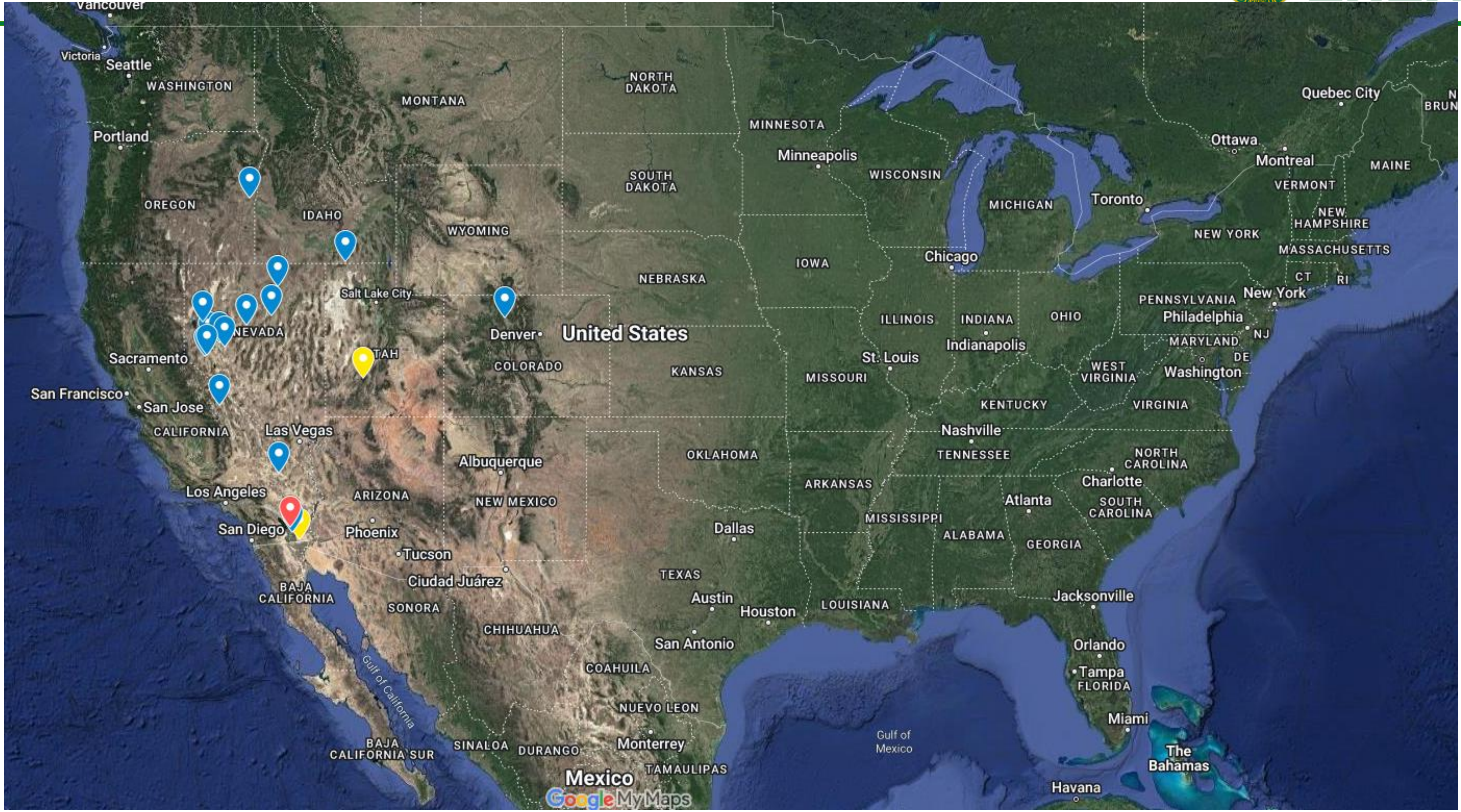
Mine Wastes

- Tailings
- Waste Rock
- Rock – Ore Ratio (USGS) Publications
- USGS
- Peer-Reviewed Literature
- Developing Estimates

Produced Waters and Leachates

- **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. https://doi.org/10.5066/F7J964W8
- "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



Lithium – USGS Produced Waters Database

Domestic Sources of Li - Google My Maps   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.   Lithium extraction from oilfield brine (utexas.edu)

- 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.

Other Non-Traditional Sources

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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 – Doug Hollett from DOE Leading This Effort

Arctic Region

- www.arctic.gov 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

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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

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Questions

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