There are numerous abundant waste and byproduct materials that could potentially serve as sources for critical materials.

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

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Modern societies generate extraordinary varieties and quantities of wastes and byproducts. By applying principles of circularity and waste minimization, we can take something that would be an environmental hazard and turn it into a resource. A few such wastes that could serve as feedstocks for recovery of metals are coal ash, acid mine drainage, petroleum coke, mine and smelter wastes, asbestos tailings, red mud, produced waters, municipal solid wastes, municipal sewage sludge, e-wastes, garnet waste abrasives, and phosphogypsum waste. The possibility of recovering valuable metals from these abundant wastes is being investigated by the US Department

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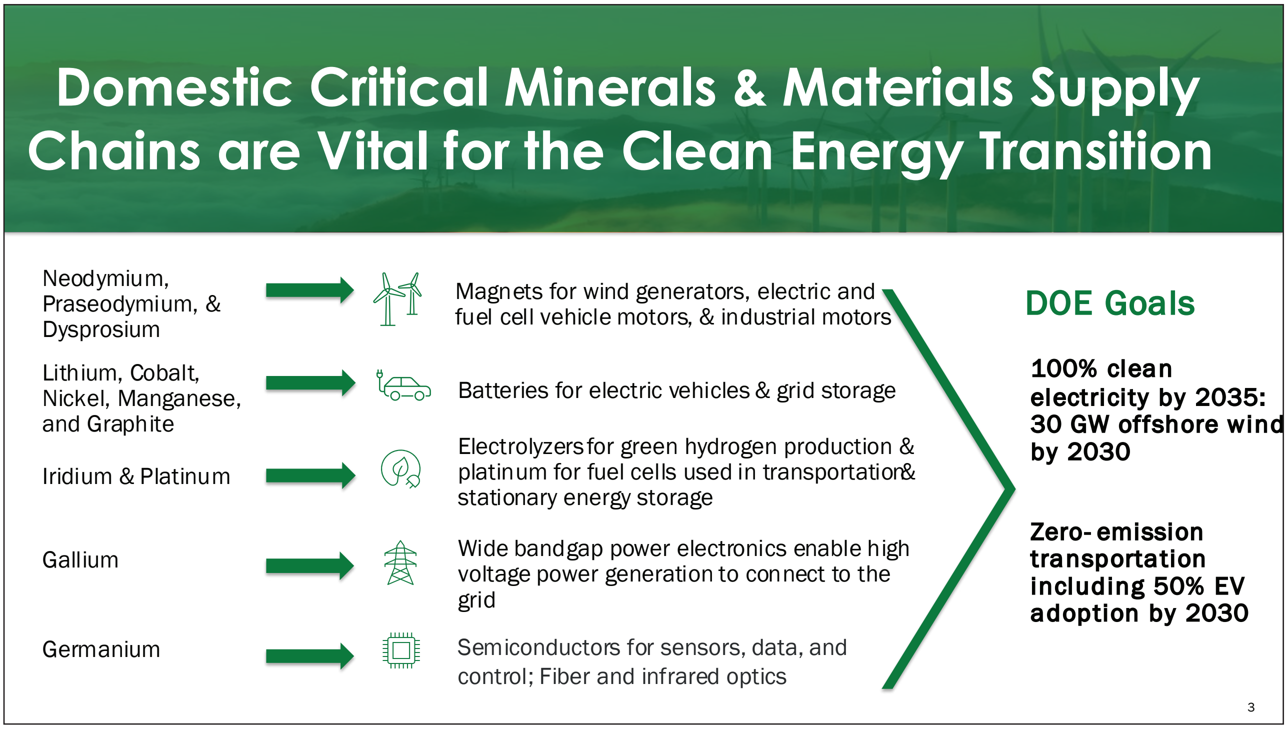

FIGURE 1 The dynamic dozen.

of Energy (DOE). However, to be of greatest value, and to help ensure the materials are used and not discarded, the mineral resources in these feedstocks need to be abundant enough to warrant investing in recovery and reclamation efforts. Metals and materials of interest, dubbed as the "dynamic dozen" for their importance in clean energy and semiconductors, are neodymium, dysprosium, praseodymium, lithium, graphite, cobalt, nickel, manganese, iridium, platinum, gallium, and germanium. A quick exploration of several potential waste feedstocks suggests that the available rare earth element and critical mineral content is ample enough to justify exploration and development activities on a large scale.

Introduction

Critical materials are defined by the Energy Act of 2020 as any nonfuel mineral, element, substance, or material that the secretary of energy determines: (i) has a high risk of supply chain disruption; and (ii) serves an essential function in one or more energy technologies, including technologies that produce, transmit, store, and conserve energy; or are a critical mineral as defined by the secretary of the interior. There are currently fifty materials listed as critical minerals; these are typically metals that are important to the US economy and imported in large quantities. The DOE has developed a subset of twelve of these materials, dubbed as the "dynamic dozen." These materials are neodymium, dysprosium, praseodymium, lithium, cobalt, nickel, manganese, graphite, iridium, platinum, gallium, and germanium, and are crucial for future clean energy and transportation systems such as renewable wind and solar power generation, electric vehicles, and hydrogen fuels, as shown in figure 1.

During the large-scale thermal roasting of ores, combustion of coals, and distillation of petroleum, a happy accident occurs. Elements partition according to their volatility (melting and boiling points of the elements and common compounds), with the highly volatile elements (such as the pollutant elements – halogens, mercury, and sulfur) often going up the stacks with the flue gas, and the less volatile elements concentrating in the solid byproducts such as ashes, flue dusts, slags, and cokes. This phenomenon allows elements of economic importance, such as the dynamic dozen, to concentrate in numerous solid waste materials resulting from large-scale thermal processing such as roasting or combustion. The concentration of these elements in abundant byproducts suggests their use for metal recovery.

The characteristics of wastes and byproducts of interest for recovery of critical materials include being abundant, accessible, preferably currently produced, having opportunities for environmental remediation, being easily extractable, and having multiple potential salable products that can be recovered. A few of these wastes are briefly discussed below.

Wastes and Byproducts from Large-Scale Thermal Processes

Coal Ash

There is approximately 2 billion tons of coal ash residing within over 1,000 impoundments scattered across the United States. The combustion process allows the coal-burning power plants to serve as large-scale concentrators of many critical elements that are present within coal. Preliminary estimates have been made for the quantities of critical elements contained within the stored ash. Table 1 shows the estimated quantities for selected metals of interest. These represent significant potential supplies, at current rates of consumption, as shown in table 2.

TABLE 1 Estimated quantities in US legacy coal ash

Critical Metal	Estimated Mass
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

TABLE 2 Potential supply in US legacy coal ash, at current rates of consumption

Critical Metal	Estimated Mass	Potential Supply (Years)
Nd	172,000 tons	40
Dy	62,000 tons	14
Li	288,000 tons	130
Co	110,000 tons	15
Ni	252,000 tons	1.1
Ir	40 tons	15
Pt	600 tons	15
Ga	20,000 tons	1,100
Ge	30,000 tons	3,900

Note that extractability of the elements of interest is also an important factor for economic recovery, and some metals may be more easily recovered from the many waste coal impoundments in the United States. It is important to note that *much larger quantities of these metals* will be needed soon to facilitate the clean energy transition.

Petroleum and Refinery Wastes

The United States refines approximately 18 million barrels of petroleum/day. It is known that heavy crudes contain valuable metals such as nickel, vanadium, and molybdenum. The heart of any petroleum refinery are the distillation units, and metals can concentrate within the high boiling fractions, and particularly in the petroleum coke. Estimates are being developed for the quantities of nickel currently produced in domestic cokes. Earlier work by the DOE analyzed abundant Alberta, Canada, oil sand process waste streams to determine the lanthanide element distributions and concentrations and suggested that these byproducts could be a source of titanium, zirconium, and some rare earth elements.

Steel Slag

Approximately 90 million tons of steel is produced every year in the United States. The slags can contain interesting concentrations of critical metals, and the quantities are being determined. Kim (2021) recently examined the potential for steel byproducts as a source for manganese, chromium, niobium, aluminum, titanium, and magnesium.

Metal Smelters

The refining of metal ores is another large-scale thermal process that concentrates valuable metals in the voluminous solid residues (flue dusts). Estimates are being made for the quantities of metals of interest that reside in the many domestic waste sites.

Other Large-Scale Solid Wastes

Mining and Mine Tailings

Mining often produces copious quantities of waste rock. The initial processing of mined ores typically involves physical separations based upon size, density, magnetic properties, and floatability (froth flotation). The reject streams from each of these processes can leave significant quantities of both the original mined metal, as well as other metals, behind. As domestic high-quality ores have been depleted over time, the cut-off grades for most metals have been reduced, so much so that many mine tailings and waste rocks now contain economically recoverable concentrations of metals. There is extensive literature on these byproducts for copper, zinc, and nickel, and Rio Tinto has made extensive efforts to recover tellurium and copper from mine wastes and tailings. It is also noted that there are over 4 billion tons of coal waste stored in many impoundments across the United States.

As we continue to collect information about these different source materials, we are better able to assess the potential for them to support domestic and worldwide critical mineral needs for the decades to come.

Red Mud

Red mud is a voluminous byproduct of aluminum production. In the Bayer Process, bauxite ore is treated with sodium hydroxide. The stoichiometry of the Bayer Process shows that 1–2 times as much red mud is produced versus alumina. Over 1 million tons of alumina are produced annually in the United States. The alkaline red mud wastes are enriched in rare earths, typically containing 0.1–1 percent rare earths by weight. Both the currently produced and legacy red mud byproducts are attractive sources for rare earths; with perhaps enough to supply annual domestic demand for rare earths, which is 10,000 tons/year. Early work on red mud is being supported by the DOE. The highly alkaline red mud also presents potential opportunities for carbon dioxide sequestration.

Asbestos

Asbestos mine tailings are highly alkaline and contain 25–30% magnesium. Researchers have proposed commercial recovery of magnesium and other valuable metals. The Vermont Asbestos Group Mine (VAG) was operational from the 1930s through 1993 and has left large quantities of legacy waste materials behind. This material could be beneficially treated to recover metals, clean-up the waste, and potentially sequester carbon dioxide.

Municipal Solid Waste

The United States produces approximately 300 million tons of municipal solid waste (MSW) annually; this translates to roughly 1 ton of MSW per person per year. The crude composition of MSW includes yard waste, food, paper, cardboard, plastics, wood, and metals. MSW can contain significant concentrations of metals, with as reported values between 1 and 17 wt%. Unfortunately, these metals are contained within a highly heterogeneous matrix. MSW ash from incinerators will contain even higher concentrations of metals and may represent a better opportunity for economic recovery.

Municipal Sewage Sludge

There is recent excitement in the research community on the elevated ppm levels of platinum group metals such as platinum, palladium, and rhodium being found in some municipal sludges. The origin of these noble metals is believed to be road dusts originating from debris from the 3-way automobile catalysts, with the dusts washing into storm drains from the rain. Some researchers have suggested the possibility of economic recovery of the platinum group metals from municipal sewage sludge.

E-Wastes

Modern society unfortunately disposes large quantities of computers, televisions, phones, and batteries, with much regrettably ending up in landfills. These devices contain most of the target metals needed for the clean energy revolution. Research is being supported by the DOE on the recovery of nickel, graphite, cobalt, manganese, lithium, and some rare earth elements from e-wastes.

Other Nontraditional Sources

Produced Waters

The commercial production of oil and gas also produces enormous quantities of produced waters. A preliminary study of domestic produced waters suggests lithium may be economically recoverable from a few of these produced waters. The DOE is initiating new research on the recovery of lithium and other valuable metals from produced waters.

Garnet Abrasives and Sands

Garnet is used as industrial abrasives, with approximately 100,000 tons produced annually in the United States. Recent work by Oak Ridge National Lab suggests the spent abrasives have high rare earth concentrations, with as much as 0.1–1% by weight total rare earth, yttrium, and scandium. The more valuable heavy rare earths and scandium are well represented in these wastes.

Acid Mine Drainage

The oxidation of sulfides present in both coals and metal ores produces waste sulfuric acid. The sulfuric acid formed will often beneficially leach valuable metals such as manganese, nickel, and cobalt from the surrounding environment. The DOE is sponsoring pilot-scale research on the recovery of manganese, nickel, cobalt, and rare earths from abundant acid mine drainage solid wastes present in West Virginia, with encouraging early results.

Phosphogypsum Waste

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.

Novel Sources

Outer Space

There are several recent start-up companies examining the possibilities of recovering valuable metals from the Moon, Mars, meteorites, and asteroids. NASA is part of intergovernmental efforts led by the DOE on "Space Mining."

Ocean and Ocean Floor

The oceans contain vast stores of many metals; unfortunately, the concentrations are typically low. For example, lithium is present in seawater at concentrations of 1 ppm. Coproduction of metals and potable or usable water could improve the economics of metal recovery. Seabed minerals present on the remote ocean floors are also being considered for future exploration. On April 28, 2023, the DOE announced potential funding for exploration of critical mineral extraction from macroalgae in the ocean. This Advanced Research Projects Agency-Energy (ARPA-E) effort seeks to study macroalgae as a potential source of critical rare earth elements.

Future work is needed on determining the optimum waste materials for recovery of critical materials, the development of improved separation techniques, the characterization of these typically heterogeneous materials, and the identification of the best products when multiple possibilities exist.

Locations and Quantities

These wastes are present broadly across the United States and North America. The figure below shows locations where many of them are prevalent in substantial quantities. For these types of wastes, a "hub and spoke" model of production and processing is a typical approach when there are several potential sources in a region, where minerals can be recovered and concentrated at the sources (spokes) and brought to a central plant (hub) for further processing. As we continue to collect information about these different source materials, we are better able to assess the potential for them to support domestic and worldwide critical mineral needs for the decades to come. Metal mining and refining byproducts, municipal solid waste, and asbestos dumps represent valuable stores of critical materials. Some locations of wastes and

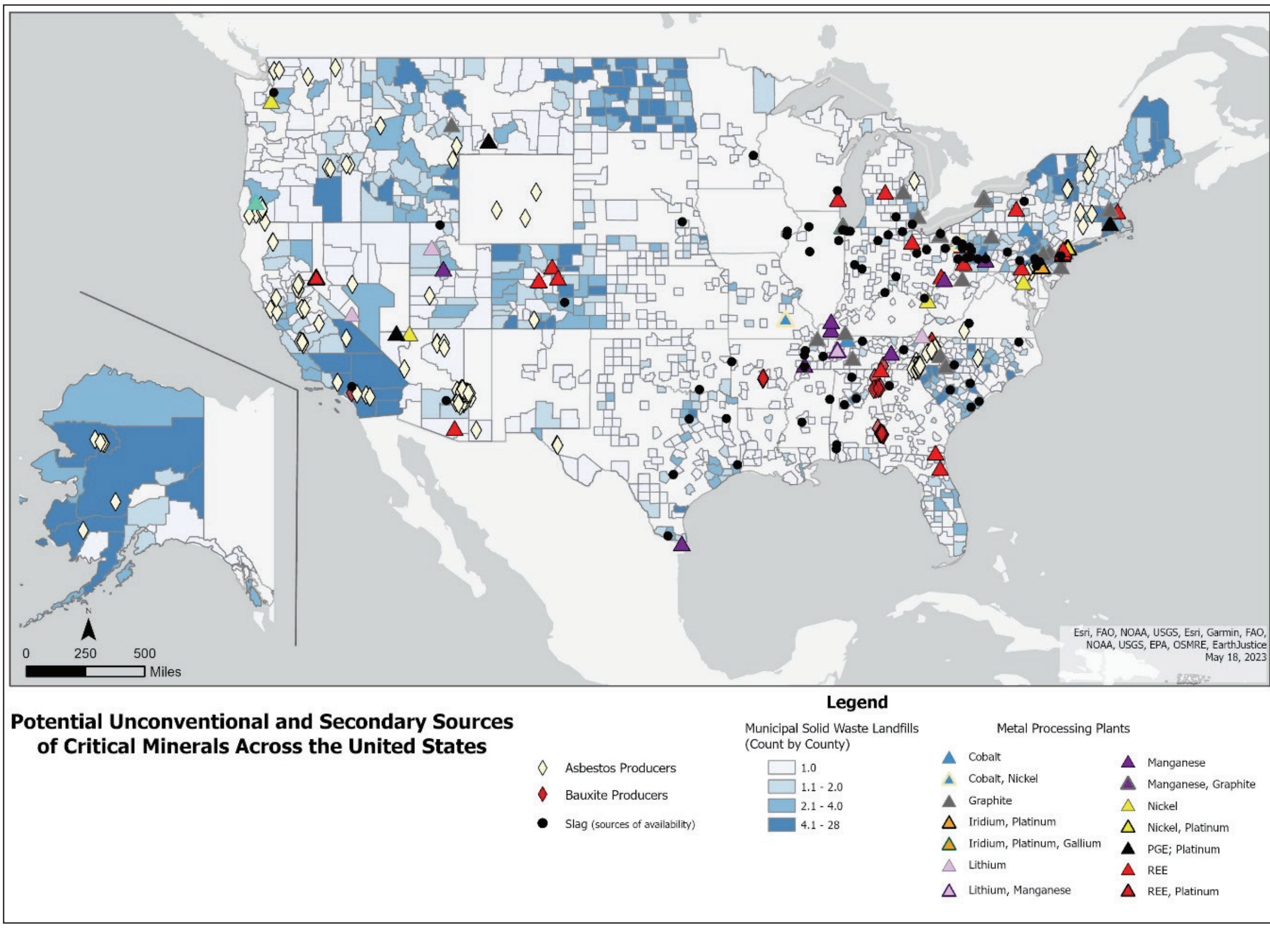

FIGURE 2 Location of select wastes and byproducts.

byproducts, along with elements present within these sites, are shown in figure 2.

The voluminous byproducts of fossil energy production and utilization are a potential resource for critical materials. The locations of petroleum refineries, coal mines, coal-fired power plants, and coal ash ponds are shown in figure 3.

Private Sector

The private sector has made significant efforts in recent years to obtain critical materials from waste materials. Numerous companies such as Alcoa, Redwood Materials, Ascend Elements, Nth Cycle, Cirba Solutions, Aqua Metals, ElementUS, Rio Tinto, and many others are targeting recovery of critical materials from abundant wastes and byproducts, using both traditional physical, thermal, and chemical separations, as well as novel separation technologies such as electrochemical and plasma methods. The DOE is spurring innovation and technology development through research efforts and funding opportunities, in collaboration with the private sector, academia, and various local and federal government agencies.

Conclusion

There are numerous abundant waste and byproduct materials that could potentially serve as sources for critical materials. These opportunities are currently being explored by the DOE, as well as the private sector, to enhance domestic security and clean up the environment. Other nontraditional and novel sources of critical materials such as produced waters for lithium recovery also merit further research. Challenges for recovery of the critical materials include the modest and often variable concentrations; ease of extraction; and development of multiple recoverable products. Future work is needed on determining the optimum waste materials for recovery of critical materials, the development of

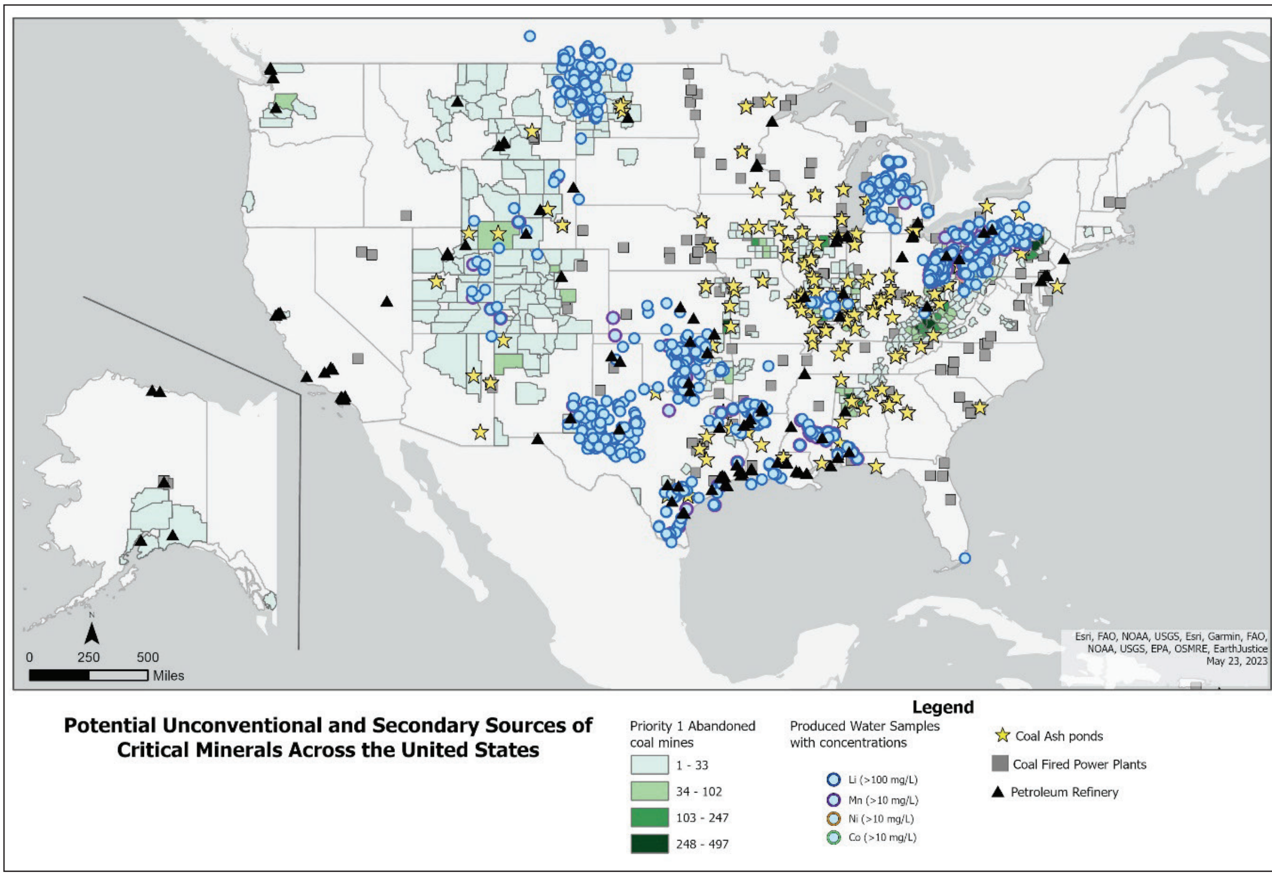

FIGURE 3 Locations of oil refineries, coal mines, ash ponds, and coal-fired power plants.

improved separation techniques, the characterization of these typically heterogeneous materials, and the identification of the best products when multiple possibilities exist. The timely and safe permitting of resource recovery from waste materials is an additional challenge that needs to be addressed.

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