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Environmental Review of Coal Ash as a Resource for Rare Earth and Strategic Elements

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ABSTRACT

Recently, prices of strategic minerals and rare earth elements have been rising dramatically due to global supply shortages and increasing demands. These metals are integral components of advanced technologies, such as, cell-phones, wind turbines, permanent magnets, and semi-conductors. The relative scarcity of these valuable elements has prompted many companies to search for new mineral sources. In addition to new mining ventures and electronic recycling programs, coal ash has been suggested as a possible large untapped resource. It is well-known that coal ash contains many common metals (e.g., Al, As, Cr, Ni, Se) but some coal ashes also contain elevated concentrations of rare earth and strategic metals (e.g., Ce, La, Ga, Ge). Several companies are exploring methods to extract rare metals from coal ash and investigating whether coal ash processing can serve as an economical and environmentally friendly alternative to traditional mining. As this new use for coal ash develops, it will be important to consider potential environmental impacts. In this presentation we explore coal ash as a source of rare earth and strategic minerals, discuss chemical extraction procedures, and highlight environmental considerations associated with these processes.

INTRODUCTION

Strategic elements encompass a broad group of metals that are essential for emerging technologies (*i.e.,* important for national defense, aerospace, and green energy industries) and have limited current and future domestic and global supplies. Several strategic metals are critical for components of energy efficient technologies (see Table 1) including rare earth elements, gallium, germanium, indium, and tellurium.[1,2] Rare earth elements are a group of chemically similar metals including the fifteen elements with atomic numbers 57 through 71, plus scandium and yttrium.[3] Currently the U.S. produces limited amounts of these metals and relies on imports from other countries, primarily China. [1,2,3] Due to growing demand for these elements and the risk of supply shortages, U.S. governmental agencies have initiated programs to identify alternative metal resources.[1,2,3]

The occurrence of trace concentrations of strategically important metals in coal and coal ashes has been understood for decades.[4,5,6] However, the economics of developing these resources have not been viable until recently, with the dramatic rise in metal prices following increased demand for these unique metals.[7,8] The exploration of any new mineral resource should include a consideration of economic, social and environmental factors. Metal mine development, particularly for strategic elements, requires extensive capital investments and complicated regulatory oversight. The length of time from resource definition, completion of environmental permitting, and to production can span many years.[3,9] Further, as observed in China, if not properly controlled, beneficiation of metal ore deposits, can result in unintended environmental consequences due to the release of chemicals used during mining and improper mine management.[9,10,11] Coal combustion waste storage facilities offer a potential source of strategic metals that may limit some of the expenses and environmental hazards associated with typical mine development. Therefore, it is worthwhile to explore environmentally sustainable methods to leverage existing coal ash deposits. This review examines several factors related to the development of rare earth and strategic metals from coal ash resources in an environmentally responsible fashion.

Table 1. Examples of Strategic Elements and Their Applications

Element	Atomic Number	Example Technology Applications[1,2]
Selected Rare Earth Elements		
Yttrium [Y]	39	Phosphors, Metal catalysts
Lanthanum [La]	57	Electric vehicles, Phosphors
Cerium [Ce]	58	Electric vehicles, Phosphors
Praseodymium [Pr]	59	Permanent magnets, Electric vehicles
Neodymium [Nd]	60	Permanent magnets, Electric vehicles
Europium [Eu]	63	Phosphors, Light-emitting diodes
Terbium [Tb]	65	Phosphors, Electric vehicles
Dysprosium [Dy]	66	Permanent Magnets, Vehicle Batteries
Other Strategic Elements		
Gallium [Ga]	31	Photovoltaics, Semiconductors
Germanium [Ge]	32	Fiber-optics, Semiconductors
Indium [In]	49	Photovoltaics, liquid crystal displays
Tellurium [Te]	52	Photovoltaics, thermoelectronic devices

Note:
This list is limited to a selected group of elements that are the focus of this review and it is recognized that a number of other metals are also considered critical for emerging technologies but are beyond the scope of this study.

TRACE ELEMENTS IN COAL ASH

The examination of trace elements in coal and coal combustion products has been documented by a number of authors.[4,5,6,7,12-16] Raw unprocessed coal contains a variety of metals, and in some cases, enriched concentrations of some strategic elements (Table 2). Surveys of coal resources indicate that some coal deposits may contain economically viable concentrations of rare elements.[7] In addition, the combustion process results in the enrichment of metal concentrations in the coal ash wastes, often several times the concentration found in raw coals (Table 2). While some metals may leach from coal ash wastes (*e.g.*, As, B, Se), many strategic metals remain bound to the ash residues (limiting their environmental mobility).[17,18] The ranges of strategic metal concentrations in some coal ashes are similar to those from mineral ores, suggesting that coal ashes are possible resources for metal recovery.[3,7]

Limited information exists to characterize the concentrations of strategic elements in U.S. coal ash storage facilities.[7,14] One detailed assessment of rare earth elements in coal ash from a Kentucky power plant reported a range of 1213.6 – 1667.6 mg/kg total rare earth elements (TREE) in fly ash and 1202.5 mg/kg TREE in bottom ash.[14] Seredin and Dai (2012)[7] estimated that the rare earth ash content from the Kentucky plant and other international coal ashes contained concentrations within the range of mineral ore deposits. Thus, the potential for utilizing coal combustion products as a source for strategic elements is evident. However, due to the lack of trace element data, there is a need to characterize strategic element concentrations in domestic coal combustion storage facilities. Further, it will be necessary to evaluate and prioritize these resources to focus efforts on those deposits with the highest amounts of strategic elements and those that can be effectively extracted from the coal ash matrix.

Table 2. Mean and Range of Concentrations (mg/kg) in Coal and Coal Ashes

Element	Raw Coal [a]	Coal Ash [b]	Coal Fly Ash [c]
Ce	20.9 (0.79-790)	468.78 (151-1784)	-- (405-565)
Dy	2.09 (0.11-28)	61.54 (18-527)	-- (32.1-50.3)
Eu	0.28 (0.025-5.8)	7.64 (2.00-31)	-- (3.9-5.9)
La	9.09 (0.07-230)	259.85 (60-839)	-- (206-286)
Nd	8.48 (0.47-230)	236.02 (70-967)	-- (183-256)
Pr	4.81 (0.17-65)	59.02 (17-239)	-- (49.0-68.4)
Tb	0.54 (0.01-21)	10.29 (3.00-80)	-- (4.9-7.3)
Y	8.18 (0.10-100)	408.34 (94-3540)	-- (191-259)
Total REE	54.9 (0.20-1031)	1723 (721-8426)	-- (1213.6-1667.6)
Ga	5.24 (0.044-41)	limited data	-- (212-299)
Ge	4.23 (0.007-220)	-- (<10-1841)	-- (1.00-356)
In	0.71 (0.025-23)	limited data	limited data
Te	1.82 (8.8-510)	limited data	-- (0.14-2.7)

Notes:
[a] Data represents detectable concentrations from unprocessed coal samples collected throughout the U.S. from 1973 to 1989 as summarized in the USGS COALQUAL.[12]
[b] Rare earth metal content estimated (from laboratory analyses) for ashes from coal deposits in the U.S., Russia, China, and the Middle East summarized by Seredin and Dai (2012).[7]
[c] Range of concentrations measured from coal and coal fly ashes collected from power facilities in the U.S., Europe, Mexico and Spain.[13,14,15,16]

RECOVERY OF STRATEGIC METALS FROM COAL ASH

The recovery of metals from mineral ores, particularly strategic elements, is a complicated multi-step process that consumes energy and results in a variety of waste products.[3,9,19] This beneficiation process includes initial crushing and grinding of the ores to smaller particles, filtration and flotation to remove undesired minerals, and further conditioning prior to final metal purification.[3,9,20] By contrast, initial metal recovery from coal ash may be more efficient than ore processing since the physical form is more amenable to processing (*i.e.*, with limited initial conditioning). Methods for extraction and separation of individual strategic metals from fly ash are emerging and becoming more efficient as chemical engineering techniques are improved.

Several extraction techniques have been summarized for strategic metals.[8,14,19,21,22,23] Generally, these processes include initial acid leaching of ash material, followed by removal (*e.g.*, precipitation) of undesired minerals, and purification using solvent extraction. The leaching stage employs the use of low-pH acids (*e.g.*, hydrochloric, nitric, sulfuric, or oxalic acid) and varying temperatures and leaching times, depending on the composition of the fly ash. After leaching, removal of non-target minerals (*e.g.*, silicates, iron, calcium) can be conducted using chelating resins or other precipitates (*e.g.*, calcium sulfate). Finally, the individual metal (*e.g.*, Ga or Ge) is purified from solution using chemical extraction solvents. Extraction efficiencies can vary (*e.g.*, 50-99%) depending on concentrations of other elements in the fly ash or due to the non-specific nature of some acids and extractants.[14,21] Chemical separation of rare earth elements can be more cumbersome. Due to the unique chemical similarity between this group of elements, multiple physical and chemical extraction techniques are typically employed to purify each metal.[19] Therefore, it is necessary to optimize the extraction technique for each coal combustion product source.[8,23]

ENVIRONMENTAL CONSIDERATIONS

Pursuit of coal combustion residuals as a resource for strategic elements should be balanced with consideration of potential environmental benefits and impacts. While rare earth and other strategic elements are necessary components of energy efficient and sustainable technologies, the process by which these materials are extracted results in the generation of multiple waste streams. If these new waste streams are properly managed, it should be clear that the development of coal combustion residues for strategic metals may provide an environmentally sustainable option to reduce the amounts of CCP wastes in storage facilities. Thus, the management of wastes remains a necessary component of metal resource development. Key issues that should be considered during this process are discussed below.

Similar to mineral ore extraction, coal ash resource recovery requires the transport and storage of feedstock for the metal separation facility. It is likely that the metal extraction facility may not be located near the coal ash resource, therefore, it will be necessary to safely transport and store coal ash residuals in a manner that limits unintended spills or leaching of contaminants. Further, since coal ash is comprised of fine particles, limiting the generation of fugitive dusts will be necessary. These issues are already present under typical coal ash storage scenarios and therefore existing engineering controls could be modified to serve this new industrial use.

Metal extraction and recovery, as described above, is a chemically intense process.[9,19] Specifically, the metal separation steps will require the use of leaching acids, caustic precipitates, and organic solvents.[9] Each of these chemical components will need to be strictly maintained to limit unintended environmental releases or exposure to the facility operators. During metal extraction, multiple secondary waste streams are generated. Metal processing requires large volumes of water for the acid leaching stages.[9,19] While some of the water may be recycled and re-used, a portion will need to be treated for contaminants. For example, coal ash residuals contain many trace elements (other than strategic elements) that are potentially toxic (*e.g.*, As, Hg, Se).[24] The initial acid leaching process is generally non-specific to trace elements, therefore any remaining common elements will require recovery and disposal. Further, any residual naturally occurring radioactive or organic wastes (from acids, extraction solvents) will also require recovery and disposal. Since, the retrieval of strategic metals from coal ash is still evolving and will need to be tailored to the specific characteristics of the coal ash source, the composition of the waste materials are likely to vary considerably. Further, these processes have yet to be commercialized, thus our understanding of future waste streams is limited.

Finally, the industrial capacity within the U.S. for production of strategic elements has been limited for decades, as these metals are predominantly imported from foreign sources.[1,2,3] In this regard, existing environmental regulations are generally limited for this industry. Specifically, occupational and environmental health standards have not been developed for most strategic metals or the specialty extraction solvents. This is largely due to limited information on the toxic effects of strategic metals on public health and ecosystems.[9] Further, the health and environmental effects from the release of these metals into the environment from all phases of development (processing, use, and disposal) is not well understood.[9] Therefore, as this industry is expanded in the U.S., further research efforts may be required to generate the necessary toxicological information to develop safety recommendations. In addition, the potential for exposure (*i.e.*, to workers, communities, or surrounding ecosystems) to any of the chemical contaminants inherent in this process is unknown, therefore, monitoring of environmental exposures may be needed as coal ash resources are reclaimed.

CONCLUSIONS

The future of advanced technologies and sustainable and efficient energy generation is dependent on the availability of a number of strategically important elements. The U.S.'s reliance on foreign sources for these elements may limit our technological capabilities and competitiveness. One possible untapped resource that may alleviate supply risks for strategic metals is our significant availability of coal combustion waste products from coal fired power plants. A number of research organizations are currently evaluating the processes to recover these strategic elements from coal ashes. As part of these investigations it is necessary to consider the environmental risks associated with developing this resource. There are several potential contaminant waste streams that are associated with the processing of metals, however, our understanding of environmental exposure and resulting health and environmental risks with coal ash metal recovery is very limited. Additional research and assessment recommendations are provided to aid coal producers with determining an environmentally sustainable path forward to developing strategic element resources from coal combustion products.

- Limited existing information is available to characterize the strategic element composition of existing coal ash storage facilities. Further efforts should be initiated to survey and identify the coal ash deposits that are economically viable for metal recovery.
- Coal combustion product deposits that are identified as being potentially economically viable should undergo a full chemical characterization to determine which contaminants may require specialized waste handling measures. In addition, this characterization can be used as one metric to prioritize those

resources that have minimal concentrations of hazardous substances that require treatment and disposal.

- Further research and development is required to optimize the metal recovery and extraction process to minimize the use (or maximize recycling) of hazardous acids and solvent extractants.
- Additional assessment of the public health and environmental risks of contaminants generated from coal ash processing should be undertaken. Specifically, additional data gathering on the toxicological effects from exposure to strategic metals or the chemicals used in their production would allow for informed development of safety recommendations.
- Finally, a thorough understanding of the potential routes of exposure and exposure concentrations generated during the various stages of coal ash processing is needed to protect occupational, public and environmental health.

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