

Program on Technology Innovation: Alternative and Innovative Technologies for Coal Combustion Product Management

2016 TECHNICAL REPORT

Program on Technology Innovation: Alternative and Innovative Technologies for Coal Combustion Product Management

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ABSTRACT

In recent years, there has been a plethora of new, modified, and revived uses of coal combustion products, both in the literature and introduced to the marketplace. In this report, these products and processes are identified, assessed, and organized in a coherent way to facilitate evaluation of their efficacy as viable and sustainable applications.

Alternative and innovative technologies, in the context of this report, refer to any process or product that is not in widespread commercial use. These include processes and products that are well developed from a technology perspective but have not made significant inroads into the marketplace, as well as new processes and products that will likely require significant further development before they are commercially viable.

The technologies are grouped into broad categories to facilitate comparison. The primary criteria considered in this evaluation were technology maturity, potential market size, and applicability for using bituminous coal ash.

Keywords

Coal ash management

Coal combustion products

Fly ash

REPORT SUMMARY

Introduction

As part of the North Carolina Coal Ash Management Act of 2014 (CAMA), all generating facilities in North Carolina owned by a public utility that produce coal ash were required to perform a study of coal combustion product (CCP) uses and markets, for submittal to the Environmental Management Commission and the Coal Ash Management Commission on or before August 1, 2016. The Electric Power Research Institute (EPRI) teamed with the University of Kentucky Center for Applied Energy Research (UK CAER) and Golder Associates to perform research on CCP use markets and technologies and provide technical support for Duke's efforts to evaluate increased CCP use as specified under the legislation.

The research was divided into three phases that parallel the studies required by the CAMA legislation:

- **Phase 1—Market Assessment.** The market assessment focused on well-established, conventional products and markets, such as concrete, cement, road construction, and reclamation.
- **Phase 2—Beneficiation Technologies.** This phase explored commercial beneficiation technologies to improve ash characteristics for use in conventional applications assessed in Phase 1.
- **Phase 3—Alternative and Innovative Technologies.** This phase identified products and technologies that currently have a limited market, or no market, in the United States.

This report provides the results of the Phase 3 identification of alternative and innovative technologies for using coal ash. The objectives of Phase 3 are to identify, categorize, and describe alternative and innovative technologies and products for the use of coal ash.

Approach

Alternative and innovative technologies refer to any process or product that is not in widespread commercial use. They may include processes and products that are well developed from a technology perspective but have not made significant inroads into the marketplace, as well as new processes and products that will likely require significant development before they are commercially viable. Technologies that are well developed but not widely used are included because they may become more important in the future as a result of improvements in the technology, changes in economics, and increased acceptance in the construction and manufacturing sectors.

Information in this report is based largely on literature and Internet searches, industry and vendor contacts, and an Open Innovation Search process. The technologies are grouped into broad categories to facilitate comparison. The discussion centers on technology maturity, potential market size, and applicability for using bituminous coal ash. The bituminous coal ash focus reflects the origin of the study in North Carolina, where bituminous coal is the predominant fuel source.

This report includes 18 technologies and more than 50 products. The vendors/researchers listed herein do not encompass all possible sources, but instead are intended to be a representative cross section of technologies. The purpose is to provide a starting point for identifying promising technologies and understanding their technical readiness. There is no intention to claim that this represents a complete list of fly ash products, vendors, or research organizations, nor should this be construed as an endorsement of a specific vendor or product. This report provides a brief overview of the technologies and products, and is intended to serve as a framework that can be expanded as additional information, products, and vendors become available.

Because sustainable markets for these technologies are not fully developed, they will require greater time and financial commitment by the power company. Development of commercial markets for alternative and new ash-based products typically takes a long time, particularly if the technology is competing with an existing, well-established commercial technology. There are several examples over the past two decades of sound technologies with significant capital backing that have failed to achieve sustained commercial success in the United States. Most of the technologies will require a commitment to working with the vendors to develop the products, obtain regulatory approvals, and communicate with end users to stimulate the nascent markets.

The technologies are discussed under the following five major categories:

- Concrete and Masonry Products
- Geopolymers and Alternative Cements
- Fillers, Extenders, and Tougheners
- Metals Extraction
- Other

Each technology description includes a brief overview, summaries of specific vendor/researcher products, and an assessment of market readiness.

Technology Groupings

Each of the 18 technologies was placed in one of four groups based on the authors' assessment. The primary consideration distinguishing the first three groups was technical maturity and market development, which together represent a measure of how much investment will be required and how quickly the products can be commercialized. Within each group, the technologies were further ordered by potential market size and value. The fourth group represents technologies that are either very early-stage technologies requiring significant basic research and development (R&D), or products that are developed technically but have failed to gain sustainable traction in the U.S. market.

Group 1: Market-Ready Technologies

This group includes technologies that have penetrated existing markets in the United States to some degree, and require no basic research. Some product testing will be required to demonstrate and customize the applications for specific ash and market areas. In general, these applications are market limited rather than technology limited. These are primarily examples of specialty concrete products and fillers, of which there are many variations beyond those listed here. This is the lowest-risk group and may require little or no R&D investment by the power company. They may be pursued with established marketers to explore the potential in a region. The markets for these products range from moderate to very small.

Flowable Fill and Foamed Concrete. The technology for flowable fill and foamed concrete is well developed, with significant existing vendor experience and flexible ash specifications. However, it appears that there is room for growth. These products generally tolerate a larger range in ash quality than conventional concrete. Increasing use of fly ash may be achieved by working with existing concrete vendors to identify market potential, establish applications, and engage end users. This alternative use requires little investment and is low risk. Addressing the quality control requirements for end users may help increase the sales of fly ash in this market.

Cenospheres and Ultra-Fine Fly Ash. The market for selling cenospheres and ultra-fine materials is relatively small but is of high value. Both products require processing of the bulk fly ash. Cenospheres are typically harvested as “floaters” from ash ponds because of their low specific gravity. As ponds are closed, separation from dry bulk ash will be much more costly and difficult. For ultra-fine products, beneficiation (size reduction, reducing carbon content) and strict quality control to ensure uniformity are required. Although the products are well understood and are of high value, they represent a relatively small market for fly ash.

Superpozzolans. Similar to ultra-fine particles, this is a high-value product with a small market. The technology is well developed, and can be pursued through discussions with an established concrete vendor at no investment cost for the power company. However, it accounts for only a very small volume of fly ash under current market conditions.

Group 2: Mature Technologies

This group consists of products that are well developed technically and have demonstrated some market potential in the United States. They do not require basic research, but generally may require some R&D to further develop, test, and/or demonstrate the products. These products are typically entering existing markets for similar materials that do not use ash as a raw material. Accordingly, the primary market development activities are aimed at demonstrating equivalent performance at a lower cost, or better performance at a similar or slightly higher cost. Vendors may be well-established companies, or they may be smaller startups seeking partnering opportunities. Development of these technologies and products represents a moderate risk and R&D investment.

Manufactured Aggregates. Many processes for manufactured fly ash aggregates have been developed in the past. They have achieved some degree of commercial success, but have generally not been a sustainable product, likely due to the low cost of natural aggregates. Manufactured aggregates can be produced from either Class F or Class C fly ash with variable quality. Despite the simplicity of the technology and the large potential market, unless the aggregate production costs are subsidized, this option is probably not cost competitive in areas where low-price natural aggregates are available.

Geopolymers. The current market for geopolymers in the United States and worldwide is limited but growing. Current uses in the United States are primarily precast products and retrofit liners for repair of sewage pipes. Some new attempts are being made to commercialize geopolymer-based lightweight masonry products. Geopolymer products have many desirable performance characteristics relative to conventional concrete, especially in high-temperature and highly corrosive environments. However, the infrastructure is not in place to support widespread adoption, especially for cast-in-place applications now dominated by the ready-mixed industry. It is expected that the geopolymer industry will continue to grow incrementally as the products become more flexible and adapted to the U.S. market. These products have the potential to use large volumes of Class F fly ash.

Masonry Units. Several technologies to produce bricks and pavers using both Class F and Class C ash types have been developed in the past. However, there appear to be market barriers to significant commercial growth in the United States. The recent liquidation of CalStar Products is the latest example of an apparently successful technology failing to sustain itself commercially. Several vendors in the United States have fly ash brick technologies, and the use of fly ash bricks and blocks is growing outside the United States, especially in India. Continued evaluation of brick and paver products is warranted, given the potential for using large quantities of fly ash; however, the past failures to gain a sustainable foothold in the U.S. market suggest a degree of risk.

Alternative Cements. Alternative cements have the capacity to use more fly ash than conventional concrete. Alternative cements typically use little or no portland cement, and often contain additional components such as limestone or ground glass, and/or proprietary additives. Alkali-activated cements are one category of alternative cement. They are generally described by vendors as having similar or better performance in concrete than portland cement. Like geopolymers, widespread use of alternative cements in the United States is limited because of difficulties in integrating new materials and nonstandard processes into the ready-mix supply chain. Alternative cements appear to have less potential for use of bituminous coal fly ash than geopolymers.

Asphalt. Although the use of fly ash in asphalt is a well-established technology, there has been very little market penetration to date. Increasing use will require actively working with suppliers and end users on a regional basis, and will likely require local demonstrations of asphalt mixing and performance of paved surfaces. If successful, asphalt can use a moderate amount of ash that does not meet specifications for use in concrete.

Group 3: Emerging Technologies

This group includes products and technologies that have potential for large or high-value markets, but will likely require a significant investment in basic research and market development. These are farther from commercialization than Group 2 technologies, will require more investment to bring to market, and will have a commensurate level of business risk.

Wastewater Brine Stabilization/Solidification. New effluent guideline regulations require power companies to treat wastewaters from flue gas desulfurization (FGD) systems. Use of fly ash and other CCPs may represent the best alternative for solidification/stabilization of brines and high-solubility solids produced at power plant wastewater treatment facilities. Although this technology has not yet been fully demonstrated for the types and volumes of treatment brines that the power industry is anticipating, there is a concerted effort by the industry and vendors to develop viable solutions quickly as ash ponds are phased out. This application has the potential to use significant quantities of CCPs while reducing salt and trace element release from both media.

Metal Matrix Composites. This technology has been available since the 1990s; however, commercialization is limited. Further R&D to facilitate product development and acceptance is required. This is a high-value use, but the fly ash volumes likely are not large, and significant preprocessing may be required. The progress of current R&D efforts should be monitored, as well as the success of early commercialization efforts in the United States and Australia.

Proppants. Proppants are a relatively new product, consisting primarily of quartz sand particles used to stabilize wells and hold fractures open in the production of shale gas and oil by fracking technology. Research is advancing on the use of processed fly ash in lieu of natural sand proppants. Because of the increasing reliance on fracking in the United States, this use has a moderate market size potential for fly ash. Additional investment in R&D is needed to demonstrate the performance and cost of fly ash in the proppant marketplace.

Polymer Composites. Fly ash polymers can be used as flame retardants in organic foams used as insulators, replacing traditional retardants based on halogenated organic compounds. They can also be used in more familiar building applications, such as roofing, siding, decking, chair rail moldings, and decorative pieces. These products are at the early research stage and not yet commercial, and they will require investment in R&D and market development. These have the potential to use small to moderate ash volumes for high-value applications.

Group 4: Technologies with Limited Current Market Potential

Technologies in this group may be technology limited or market limited. In either case, these are considered the most difficult to commercialize in the short term. Market-limited technologies may be well developed technically but have shown an inability to gain acceptance in the United States. That does not preclude their future acceptance, but suggests that there may be underlying market constraints. The technology-limited products are in early-stage development and will require substantial R&D investment. They are considered to be at least five to ten years or more from commercial implementation and may never be economically feasible.

Autoclaved Aerated Concrete (AAC). Although the technology is mature and well accepted outside the United States, there is little or no market in the United States. The potential market for fly ash in AAC products could be moderate to large if these products attain industry and public acceptance, but there are no current indications that such a scenario will occur soon.

Zeolites and Water Treatment. The chemistry to process fly ash into zeolites is well understood, but fly ash zeolites have been unable to compete with natural zeolites on cost and other synthetic zeolites on quality. As a result, the advantages of using fly ash are not clear and there is limited market potential at this time. However, there continue to be ongoing R&D and product development, particularly in the area of water treatment.

Metals Recovery. This group of technologies has been the subject of speculation and research activities for more than 20 years. There is limited activity in the United States at this time. Recovery of alumina and magnesium is currently being actively researched outside the United States, particularly by the Chinese government. This market is largely driven by worldwide commodity prices. One significant barrier in the United States is management of the large amount of waste produced by these operations.

Rare Earth Element (REE) Recovery. Recovery of REEs from fly ash is at the early research stage and will require significant investment in R&D and a change in market conditions before it is commercially feasible. REEs are present in fly ash in trace quantities, and management of wastes generated during their recovery is a significant concern. It is unlikely that a commercially viable process will emerge in the near term under the current supply and demand conditions. However, as evidenced by the market volatility over the past decade, market conditions can change rapidly for this commodity. The Department of Energy has the lead in this relatively high-cost R&D seeking to identify and demonstrate feasible technologies.

Nanotechnology. Nanotechnologies in general are a very active research area, and may be applied in various fly ash products. One proposed application includes the use of a fraction of fly ash to enhance heat transfer in nanofluids. This technology is at the very early R&D stage, and even when fully developed will likely use only a very small fraction of ash. However, given the large research interest in nanoparticles, this area warrants tracking for future high-value applications.

Plasma Arc/Vitrification Processes. Vitrification has been proposed to reduce leaching of fly ash, with subsequent use of the glassy material for various products, such as manufactured aggregates and rock wool insulation. It is also proposed as part of a process to extract REEs from fly ash. It is relatively costly, and plasma arc and vitrification technologies are unlikely to be an economical alternative for the sole purpose of creating fly ash products.

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PRIMARY AUDIENCE: Utility personnel in charge of planning and managing coal combustion products

KEY RESEARCH QUESTION

In recent years, there has been a plethora of new, modified, and revived uses of coal combustion products (CCPs), both in the literature and introduced to the marketplace. In this report, these products and processes are identified, assessed, and organized in a coherent way to facilitate evaluation of their efficacy as viable and sustainable applications.

RESEARCH OVERVIEW

Alternative and innovative technologies, in the context of this report, refer to any process or product that is not in widespread commercial use. These include processes and products that are well developed from a technology perspective but have not made significant inroads into the marketplace, as well as new processes and products that will likely require significant further development before they are commercially viable.

The technologies are grouped into broad categories to facilitate comparison. The primary criteria considered in this evaluation were technology maturity, potential market size, and applicability for using bituminous coal ash.

KEY FINDINGS

- This report includes 18 technologies and more than 50 products. The vendors/researchers listed in the report do not encompass all possible sources, but instead are intended to be a representative cross section of technologies. The purpose is to provide a starting point for identifying promising technologies and understanding their technical readiness.
- The technologies are discussed under five major categories: Concrete and Masonry Products; Geopolymers and Alternative Cements; Fillers, Extenders, and Tougheners; Metals Extraction; and Others. Each technology description includes a brief overview, summaries of specific vendor/researcher products, and an assessment of market readiness.
- Most of the technologies in this report will require a commitment to working with the vendors to develop the products, obtain regulatory approvals, and communicate with end users to stimulate the nascent markets.

WHY THIS MATTERS

Utilities dealing with large amounts of coal ash, both fresh and stored, must constantly address, judge, and evaluate technologies to use the ash. This report organizes and assesses new and innovative technologies based on their technical maturity, market development, potential market size, and value

HOW TO APPLY RESULTS

The technologies identified in this report represent a good cross section of alternative and innovative coal ash applications, but the list is not intended to be comprehensive. New or modified ash use applications are appearing regularly as the industry adjusts to changing market conditions and R&D continues to improve on existing products and develop new ones. This framework was constructed to allow updating and revision on a regular basis, as promising new technologies and processes are identified or as market conditions change.

LEARNING AND ENGAGEMENT OPPORTUNITIES

- Program 78 on Coal Combustion Product Use includes identification and testing of new and evolving technologies with potential for high-volume CCP use.

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PROGRAM: 78, Coal Combustion Product Use

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1

INTRODUCTION

Background

As part of the North Carolina Coal Ash Management Act of 2014 (CAMA), all generating facilities in North Carolina owned by a public utility that produce coal ash are required to perform a study of coal combustion product (CCP) uses and markets, for submittal to the Environmental Management Commission and the Coal Ash Management Commission on or before August 1, 2016. The components of the requirements listed in the CAMA legislation, as found in Part 3 Section 4(e) of the bill, which can be found online at <http://www.ncleg.net/Sessions/2013/Bills/Senate/PDF/S729v6.pdf>, are as follows:

1. The carrying out of a market analysis for the concrete industry and other industries that might beneficially use CCPs.
2. The study of the feasibility and advisability of installation of technology to convert existing and newly generated CCPs to commercial-grade CCPs suitable for use in the concrete industry and other industries that might beneficially use CCPs.
3. An examination of all innovative technologies that might be applied to diminish, recycle or reuse, or mitigate the impact of existing and newly generated coal combustion residuals.

Duke Energy is a principal producer of electricity in North Carolina, with approximately 10 GW of coal-fired generation. The Electric Power Research Institute (EPRI) teamed with the University of Kentucky Center for Applied Energy Research (UK CAER) and Golder Associates to perform research on CCP use markets and technologies and provide technical support for Duke's efforts to evaluate increased CCP use as specified under the legislation. This research focused primarily on coal ash, because Duke currently markets a large percentage of its flue gas desulfurization gypsum.

A rational utilization strategy includes maximizing and expanding existing conventional uses, and developing new and innovative applications in order to expand the overall market potential. A comprehensive strategy should consider the potential for using newly produced (dry) ash as well as the processing and recovery of ash stored in ponds. It is also important to consider the environmental performance of these applications along with their engineering performance.

The research was divided into three phases that parallel the studies required by the CAMA legislation:

- **Phase 1 – Market Assessment.** The market assessment focused on well-established, conventional products and markets, such as concrete, cement, road construction, and reclamation.
- **Phase 2 – Beneficiation Technologies.** This phase explored commercial beneficiation technologies to improve ash characteristics for use in conventional applications assessed in Phase 1.
- **Phase 3 – Alternative and Innovative Technologies.** This phase identified products and technologies that currently have a limited market, or no market, in the United States.

This report provides the results of the Phase 3 identification of alternative and innovative technologies for using coal ash.

Objectives

The objectives of Phase 3 are to identify, categorize, and describe alternative and innovative technologies and products for the use of coal ash.

Approach

In recent years, there has been a plethora of new, modified, and revived uses of CCPs in the literature and introduced to the marketplace. In this phase, these products and processes are identified, assessed, and organized in a coherent way in order to facilitate evaluation of their efficacy as viable and sustainable applications. A primary consideration was whether the barriers to increased application of the products and processes are imposed by technology deficiencies or market factors.

For this report, *alternative and innovative technologies* refer to any process or product that is not in widespread commercial use. They may include 1) processes and products that are well developed from a technology perspective but have not made significant inroads into the marketplace, and 2) new processes and products that will likely require significant further development before they are commercially viable. Technologies that are well developed but not widely used are included because they may become more important in the future due to improvements in the technology, changes in economics, and increased acceptance in the construction and manufacturing sectors.

Information in this report is largely based on literature and Internet searches, industry and vendor contacts, and an Open Innovation Search process described below. The technologies are grouped into broad categories to facilitate comparison. The primary criteria considered in this evaluation were technology maturity, potential market size, and applicability for using bituminous coal ash. The bituminous coal ash focus reflects the origin of the study in North Carolina, where bituminous coal is the predominant fuel source.

The Open Innovation Search used for this report resulted in some new and unexpected uses from across industries and technical disciplines that stretch beyond the power industry. In general, an Open Innovation Search can result in technologies at early technology readiness level, many times still at the basic research and development (R&D) level. This was the case with some of the technologies identified during this study, and as a consequence, this report also addresses early R&D efforts led by universities, research organizations, and start-up companies.

Vendor and Researcher Information

There are many variations on these technologies that are currently being researched or offered as solutions in the marketplace. This report includes 18 technology groupings and more than 50 vendor products. The vendors/researchers listed herein do not encompass all possible sources, but instead are intended to be a representative cross-section of technologies. The purpose is to provide a starting point for identifying promising technologies and understanding their technical readiness. There is no intention to claim that this represents a complete list of fly ash products, vendors, or research organizations, nor should this be construed as an endorsement of a specific vendor or product. This report provides a brief overview of the technologies and products, and is intended to serve as a framework that can be expanded as additional information, products, and vendors become available.

2

CONCRETE AND MASONRY PRODUCTS

Fly ash has been used in a variety of concrete products for many decades. It is well suited for these products due to its grain size and shape, chemical characteristics, and pozzolanic nature. In 2014, more than 13 million tons of fly ash were used in concrete and concrete products, representing 57% of all fly ash use (ACAA 2015).

The most common applications involve replacing 15-40% of portland cement in conventional concrete products. These applications are addressed in the companion reports, the Phase 1 Market Assessment report (EPRI 2016a) and the Phase 2 Beneficiation Technologies report (EPRI 2016b). Common applications include roads and building footings, and precast products such as bridge abutments, pipes, walls, panels, and blocks. Vendors include any companies that produce concrete construction materials. These concrete markets are well established for fly ash, both nationally and in North Carolina, and are not included in this Phase 3 report.

There are also many specialty products made using fly ash in conventional portland cement concrete applications that have not achieved similar widespread commercial success. In some cases, these products are well developed from a technology perspective and may be used in parts of the United States but are not well established in the North Carolina region. There are many variations on these products; a few examples are described in this section.

Flowable Fill and Cellular Concrete

Description

Controlled low-strength material (CLSM), or flowable fill, is a high fly ash content cementitious material that can be used in place of typical backfill material. It is often used where fill placement and compaction are difficult, such as around pipes, for abandoning underground tanks and foundation structures, to stabilize underground voids, and in road base construction. CLSM has the advantage of being easy to pump, and it flows around structures and obstructions. The material is self-leveling and self-compacting, eliminating the need for vibratory and compacting equipment. It eventually achieves the strength of a low-grade concrete, with a maximum compressive strength of 1200 psi (ACI 2013). Lower-strength mixes, not to exceed 150 psi, are used where future excavation through the material is a consideration (www.flowablefill.org).

The ingredients in flowable fill are similar to those in concrete—cement, fly ash, water, sand, and aggregate. It can be made using either Class F or Class C fly ash, and can utilize larger amounts of Class F ash as a sand replacement. Because the strength requirements are relatively low, off-spec fly ash (i.e., fly ash not meeting the ASTM C618 specification for use in concrete) can be used.

Foamed concrete, also called low-density cellular concrete fill (LDCCF), is a type of lightweight concrete that contains small air bubbles instead of aggregate such as stone and sand. Foamed concrete is a lower-weight alternative to flowable fill.

Foamed concrete is composed of a mixture of portland cement and water with a foaming agent that is designed to produce low-density mixes for geotechnical and construction projects. Because of its low weight and the low risk of segregation, cellular concrete is easily pumped long distances at low pressures.

Applications for foamed concrete include geotechnical (annular grouting, backfills, load-reducing backfills, roadway subbase, pipe and tank abandonment, pervious lightweight concrete); mining (annular applications, ground support, material transport, backfills, reclamation); and manufacturing of building materials. Mining and geotechnical applications account for the largest uses of foamed concrete. Foamed concrete also has good thermal and acoustic insulating properties.

Fly ash is used in foamed concrete as a replacement for portland cement, to reduce heat of hydration and to add flowability to the mix. Typical mixes can contain 30% to 50% of fly ash as cement replacement. However, the chemical composition of the foaming agent used normally determines the type and quantity of fly ash that can be used in the mix. Type C and Type F fly ash can be used in foamed concrete as long as the loss on ignition (LOI) level is below 5%.

Commercial Vendors

Many commercial concrete vendors can produce and use flowable fill and foamed concrete. One example in the North Carolina region is provided below.

Titan America

Winston-Salem, NC (Roanoke Cement)

http://www.titanamerica.com/products_services/ready_mixed_concrete/flowable_fill/

Titan America is a large cement and concrete company that produces a range of products. They have subsidiary companies located along the central and southeastern seaboard. They use pre-mixed products for backfill around sewer and utility trenches, bridge abutments, conduit trenches, pile excavations, and retaining walls.

Market Readiness

Flowable fill and foamed concrete are mature technologies. Both are used primarily for backfill as an alternative to compacted soil, particularly in access-limited situations. This use is well established for flowable fill, and it appears there is room for market growth. ACAA (2015) statistics indicate that about 84,000 tons of fly ash were used in flowable fill applications in the United States in 2014. There appears to be little current use of fly ash in foamed concrete.

Autoclaved Aerated Concrete (AAC) Blocks

Description

Autoclaved aerated concrete is a building material formed by combining a slurry of quick lime (or quick lime and cement) and sand (or fly ash) with fine aluminum powder in saturated steam at a temperature above 100°C (EPRI 2000). The aluminum powder reacts with the slurry, forming bubbles of hydrogen gas that expand the mixture, resulting in a very lightweight material that can be molded as building blocks and panels.

The main advantages of AAC blocks compared to conventional concrete block are a) lower thermal conductivity (i.e., higher insulation value); b) light weight; c) good fire resistance; and d) higher resistance to sulfate attack.

Aerated concrete blocks can use fly ash as replacement for sand and alumina, and therefore AAC blocks can contain large amounts of fly ash. Fly ash can represent up to 70% of the weight of these blocks. AAC blocks and panels are very popular in Europe, mainly due to their low thermal conductivity. Approximately 31% of the masonry concrete market is composed of AAC blocks and panels in the United Kingdom, accounting for 16.2% of the fly ash used in 2014 (UK Quality Ash Association 2005, 2014). Similar and even higher use rates are attained in other European countries (Schnitzler 2006).

Construction materials and construction techniques are very different in Europe and in the United States. Although introduced in the United States almost two decades ago, AAC is not currently widely used here.

Commercial Vendors

AERCON AAC
Haines City, FL

www.aerconaac.com/indexold.html

AERCON is the only AAC manufacturer with a plant in the United States that produces various sizes of panels and blocks for the construction of wall, floor, and roof systems. Their manufacturing plant is located near Haines City, Florida, and products are shipped throughout the United States.

Although AAC can have a large percentage of fly ash in its composition, AERCON does not currently use fly ash as a raw material (using sand instead) and has no plans to use fly ash in the near future.

Hebel USA
San Antonio, TX

www.hebel-usa.com/index.php#_sub2103

Hebel manufactures aerated concrete blocks at their plant in Monterrey, Mexico, and exports them to the United States. Hebel previously manufactured AAC blocks at a plant located in Adel, Georgia, that closed in 2010.

The Hebel brand is targeted to large-scale industrial end users, but in Mexico and the United States it also produces blocks and reinforced panels for residential and nonresidential construction.

Market Readiness

AAC blocks are a mature technology. However, the construction industry in the United States is very different than in Europe, and the AAC technology has not met with similar commercial success here. In 2006 there were five manufacturers of aerated concrete blocks in the United States, and that number has since decreased to only two, with one of those two having the plant located in Monterrey, Mexico, near the border with the United States.

Masonry Units

Description

Concrete bricks, pavers, and other masonry units are traditionally made from the same ingredients as conventional concrete: portland cement, water, sand, and aggregate. Fly ash can be substituted for the portland cement, sand, and aggregate, with very high replacement percentages, in some cases in excess of 80 or 90%. Fly ash can also be used as a component of traditional kiln-fired bricks.

Bricks and pavers made with fly ash were first developed more than two decades ago, but they are not commonly marketed in the United States. There have been various technologies that have been advanced for producing fly ash bricks, primarily involving a dry press process. Fly ash bricks are gaining popularity in India, primarily due to large amounts of fly ash in the country and a mandate by the government to use fly ash in bricks produced within a 60-mile radius of a thermal power plant. The National Thermal Power Corporation (NTPC) of India in particular has made significant investment in equipment to produce fly ash bricks, with capacity installed to produce more than 60,000 bricks per day (<http://www.ntpc.co.in/ash-download/1675/0/fly-ash-bricks>; http://www.ecobrick.in/resource_data/KBAS100100.pdf). Their use in the United States, Europe, and Australia, however, appears to be more limited, primarily due to industry and market constraints.

Both Class C and Class F ashes can be used for bricks and pavers. Class C can be used as the sole binder in the bricks (Liu 2005), while Class F ash fly ash usually requires another binder.

Concrete bricks and pavers are less sensitive to unburned carbon than high-strength concrete products; however, aesthetic qualities are important considerations for concrete masonry units in the United States, and high carbon content can impart undesirable color to the final product. Conversely, in kiln-fired bricks, high carbon content can enhance firing, and iron oxides in fly ash can enhance brick coloration. Fly ash impacted by dry sorbent injection used to control acid gases may not be suitable for bricks due to elevated sulfur and soluble sodium concentrations.

Commercial Vendors

CalStar Products, Inc. Recently Liquidated

CalStar was a start-up company initially located in northern California that concentrated on producing masonry products using fly ash to take advantage of the growing market for green building products. The CalStar bricks were initially formulated with more than 90% Class C fly ash in laboratory tests, but that was reduced to roughly 30-40% in a pilot production facility. The bricks and pavers were produced using a mechanical press process, and used only Class C fly ash. They were marketed as a green product that had high recycled content, consumed less energy, and had a smaller carbon footprint than traditional bricks and pavers.

In 2010, CalStar built a pilot brick-making plant in Caledonia, Wisconsin, that received fly ash from the We Energies power plant in Oak Creek. In 2013 they shipped just over 5 million units containing about 7,000 tons of fly ash (Rapoport 2013). They built a full-scale operation in Columbus, Mississippi, in 2014. Both plants were shuttered by the end of 2015, and the equipment and technology were liquidated. Headwaters, Inc. acquired the technology in early 2016.

CalStar licensed the brick-making process from Ecologic Tech (formerly Freight Pipeline Company). According to their website, Ecologic Tech is not currently seeking new licensees in the United States (Ecologic Tech 2016)

Nu-Rock Australia www.nu-rock.com/

Nu-Rock Corporation is a design and build company with a process for the production of building products and civil engineering materials from coal ash and steel mill wastes.

Nu-Rock provides the equipment to make bricks, blocks, and tiles with fly ash. The specific process for manufacturing these products includes the use of a proprietary binder and curing at room temperature. The company presented data showing very competitive prices for these products when compared with traditional products in Australia. Additionally, company data show good performance in tests for strength, permeability, and resistance to salt attack.

Nu-Rock Corporation has built a 1400-m² fully automated pilot plant in Australia for manufacturing these products. Case studies of their use in housing units in South Africa and in Sydney are also presented on the company website. Currently, the company is working toward building a manufacturing plant at a coal power station in Australia.

RamRock Building Systems, LLC Chattanooga, TN www.ramrock.com

RamRock is a start-up company that engineers and designs building systems that use urban and industrial waste as raw materials. The company has recently finished the incubation and initial proof of concept of their wall system design that uses a hydraulic press to fabricate interlocking building blocks. Their block and panel production can be customized for each individual structure.

RamRock characterizes their products as ready to commercialize.

Pittsburgh Mineral & Environmental Technology, Inc.
New Brighton, PA
www.pmet-inc.com

Pittsburgh Mineral & Environmental Technology, Inc. (PMET), in business since 1987, offers process R&D services and laboratory support to the mining, smelting, and energy industries. PMET has a patented process to produce building blocks from Class F coal ash with similar properties as clay bricks. Their process was successfully demonstrated in a project funded by the Pittsburgh Department of Environmental Protection in 2005, where a high-LOI fly ash from the Hatfield's Ferry plant in Pennsylvania and bottom ash from the Niles plant in Ohio were used to produce bricks.

The process is similar to that of autoclave aerated concrete and consists of mixing the feed materials (ash and lime), pressing the mixture into the desired shape, and curing the product in an autoclave. This brick product can contain as much as 90% fly and bottom ash with about 10% by weight of quick or hydrated lime.

PMET does not operate any production facilities, but has developed an economic model that estimates the capital and operating cost for a commercial-scale operation producing approximately 15 million bricks per year. Additionally, PMET has a facility in its laboratory capable of producing full-size bricks from various feed sources.

Eco-Ash LLC
Baltimore, MD
www.eco-ash.com

Eco-Ash is a small company that has partnered with a traditional brick-making company in the United States to produce and market kiln-fired bricks containing fly ash. The bricks are made with a press mold technology using up to 70% fly ash. Most of the testing has been done with Class F fly ash, but Class C ash can also be used. Eco-Ash has indicated that they can also use bottom ash in their process.

According to the company, the critical component of the technology is the method of stacking and loading the pressed bricks prior to conveyance into the kiln, to allow adequate firing time without slowing the curing process. The kiln is fired at 1800-2000°F. High carbon content in the fly ash facilitates the firing process, and the company claims about 40% energy savings compared to conventional clay kiln-fired bricks.

This technology is at the conceptual design phase, and no production facilities have been constructed to date. A full-scale plant would be co-located near a power plant ash source, with potential to use 50,000 tons of fly ash or more annually. The primary product would be pavers and other horizontal applications, with distribution within about a 500-mile radius. Eco-Ash has indicated that they have successfully tested the process using fly ash from United State's power plants at large test facilities in Holland and France, and that the products are cost-competitive with conventional brick products.

Vecor
Australia
www.vecor.com

Vecor Australia specializes in recycling fly ash into various building and construction products. They license a technology patented by the University of New South Wales that involves processing the fly ash through extraction in order to recover raw materials that can be used to replace sands, clays, and aggregates in a variety of products. Their product line includes pavers and bricks that are made using 80% sintered fly ash content, as well as ceramic wall and floor tiles. Vecor owns a pilot facility in China and has access to pilot test facilities in Australia and Italy.

Market Readiness

Bricks and pavers and other similar products represent a mature technology both worldwide and in the United States. They have been researched and marketed sporadically in the United States over the last two decades, but have not achieved widespread acceptance in the marketplace. Although they represent an environmentally friendly alternative to conventional bricks, there remain manufacturing and transportation barriers to greater market penetration that continue to limit their commercial growth. In most cases, brick plants would be co-located with power plants sourcing the ash. CalStar Products recently achieved modest commercial success in the United States, establishing a pilot plant and a full-scale plant dedicated to the production of masonry units using fly ash. However, their success was short-lived, as they ceased operations after less than five years of operation. Interest in the United States is primarily for pavers and decorative masonry. Worldwide there is a great deal of interest in fly ash brick technologies, especially in India and China, for use within the building industries.

Superpozzolans

Description

The term “superpozzolan” is used to describe fly ash that has been beneficiated to the point where its performance is at a level of the costlier pozzolans, such as meta-kaolin and silica fume. The level of beneficiation for the production of this kind of product is high—typically the mean particle size (d₅₀) is in the range of 3 to 5 μm, and the yield of this product is in the range of 30% to 40%. This product is typically derived from dry fly ash by air classification, often using several passes. It may be possible to derive from wet or ponded fly ash with a hydraulic separator (see Phase 2 report, EPRI 2016b).

Superpozzolans have multiple benefits. The small grain size and high surface area make them highly reactive. They also have rheological advantages, as the fly ash reduces water demand and enhances workability. This is claimed to be a distinct advantage over competitive materials such as silica fume. Although silica fume is a very strong pozzolan, its very high surface area generally has a negative rheological effect due to increasing water demand, sometimes resulting in “sticky” concrete.

Commercial Vendors

Boral Materials Technology

San Antonio, TX

<http://boralamerica.com/fly-ash>

Boral Materials has offered a commercial product, Micron³, in this category for over 10 years. It is based on the air classification of a Class F fly ash at a power plant in Texas and is shipped throughout North America. This product is marketed as an additive for high-strength concrete and precast products, and its performance is claimed to be comparable to that of silica fume (www.boralna.com/brochures/ordering/PDF/Micron3TechBulletin.pdf?pdfName=Micron3TechBulletin.pdf). Typically, high-strength concrete is made by increasing the amount of portland cement, which results in paste shrinkage issues and the need for very high-performance pozzolans. Micron³ is reported to be comparable to, or better than, silica fume for controlling both plastic and dry shrinkage.

Ash Resources Ltd

South Africa

www.ashresources.co.za

Size-classified fly ash products are also produced in South Africa by Ash Resources Ltd. Ash Resources is controlled by Lafarge of South Africa and internationally markets an extended line of products derived from fly ash. They produce conventional pozzolan for concrete application as well as a highly classified super pozzolan, SuperPozz and SuperPozz pro (www.ashresources.co.za/portfolio-item/superpozz).

Market Readiness

This is a mature technology. There is currently a small market for specialty applications in the United States and in South Africa, and there is also interest in developing this kind of product in China. It is reported to sell at levels of only about 1,000 to 1,500 tons per year in the current market. It costs much more to produce than conventional ASTM-compliant fly ash, but also commands a premium price.

Manufactured Aggregates

Description

The term aggregate refers to sand, gravel, or stone of various sizes and shapes that are used in concrete and many other construction products and activities. It is among the most widely used construction materials, and is typically mined from quarries. Fly ash can be used to produce manufactured aggregate that replaces virgin mined aggregates. This allows greater use of fly ash in concrete and masonry block products as part of the aggregate replacement, as well as use in roadbed and other construction applications.

Like masonry products, manufactured aggregates are not a new concept. The Lytag process (see below) was developed in Great Britain more than 50 years ago. There have been many processes for manufactured fly ash aggregate developed in the past under many different brand names. Most processes produced a lightweight aggregate. They typically involve a process for agglomeration of the fine fly ash particles and addition of a binder as necessary for strength development. In some cases, they may be sintered to harden the exterior of the aggregate.

Commercial Vendors

PMI Ash Technologies, LLC.
Raleigh, NC

www.pmiash.com/aardelite_aggregate.asp

PMI licensed the technology to produce an aggregate, called Aardelite, from a Dutch company. The aggregate contains up to 95% Class F fly ash primarily for use in masonry block products. Other components are lime and water. The manufacturing process occurs at normal pressures and temperatures up to 85°C, producing an aggregate that is spherical and lightweight. Aardelite does not use a sintering step, so it is less energy-intensive than other technologies. The first commercial plant using this process was built at the Crystal River power plant in Florida; it produced a total of 1.7 million tons of aggregate but has since shut down. Additional plants using this process have been constructed outside the United States.

Minergy
Neenah, WI

www.minergy.com/technology/

Minergy LLC was a subsidiary of Wisconsin Electric Power Company in the 1990s that produced lightweight aggregate from fly ash and sewage sludge. The first manufacturing facility was located near the Oak Creek power plant and continued to operate there until 1998. Minergy is now an independent company specializing in waste vitrification and other processes and products, including Minergy LWA (a trade name derived from *light weight aggregate*). LWA is produced from fly ash, sewage sludge, paper mill sludge, and clay binder. Although the product is fired in a rotary kiln, the company claims it uses less energy resources than similar products because the fly ash and sludge provide most of the fuel. Minergy does not currently have any facilities producing aggregate.

Lytag, Ltd.
England

www.lytag.com

The Lytag process for producing lightweight aggregate from fly ash was first developed in Great Britain in 1958 and has sold more than 16 million tons of product. The process agglomerates fly ash into spheres and then heats them at 1100°C to harden the exterior and produce aggregate with half the weight of conventional aggregate. A large manufacturing facility was opened near Drax Power Station in 2013.

Advanced Processes, Inc.
Ambridge PA

www.advancedprocesses.com

Advanced Processes Inc. (API) builds and supplies agglomeration equipment to change raw material and waste streams into products. API offers two approaches to reutilization of fly ash: 1) agglomeration of fly ash with additives to produce a porous aggregate; and 2) thermal processing of the agglomerate to produce a stronger and more porous product. This company has built a commercial system that recovers 90,000 tons of waste per year and has worked with several companies in the past.

Market Readiness

Manufactured concrete aggregates using fly ash are a mature technology, and they have been marketed commercially in various forms within and outside the United States. The market for aggregates as a construction material is huge, and worldwide is expected to grow at an annual rate of 5.2%, based on a recent market assessment report from the Freedonia Group (2016). The Freedonia Group also estimates that the market for alternative aggregates, including those containing fly ash, will grow at twice the rate as the market for sand and gravel. Several efforts to market ash aggregates in the United States have achieved some success, but have failed to develop into a sustainable commercial enterprise, likely due to the low cost of natural aggregates.

3

GEOPOLYMERS AND ALTERNATIVE CEMENTS

Section 2 described cementitious products based on portland cement technology that are generally well developed but lack market penetration. This section describes cementitious products based largely on alternatives to conventional portland cement concrete. These products typically use much higher amounts of fly ash, and in many cases represent a new paradigm in cementitious products. Accordingly, they face difficulties with integration into the traditional construction industry in the United States. They are largely found in precast and specialty applications at the present time. However, they offer opportunities for significant expansion of fly ash use as the products become more widely accepted.

Geopolymers

Description

Geopolymers are an alternative form of alkali-activated cement that does not use any portland cement. Geopolymer cement was first developed in the late 1970s and has been extensively researched since that time (Davidovits 1991). It consists of inorganic aluminosilicate polymers formed under highly alkaline conditions. There are several variations on the chemical synthesis of the polymers, generally consisting of a pozzolan, such as fly ash, and an alkaline activator, such as sodium silicate and sodium hydroxide. Geopolymer concrete is then produced by mixing geopolymer cement with aggregate.

Class F fly ash is preferred for geopolymers because of the higher silica and alumina content. Other ash characteristics of importance are particle size, amorphous (glass) phase present, and carbon content. Geopolymerization is facilitated by high glass content in the fly ash, while crystalline phases tend to slow the reaction rates (EPRI 2015). Silica and alumina bound in crystalline phases do not participate in the geopolymer formation.

Geopolymers have several advantages over ordinary portland cement (OPC) concrete. Geopolymer concrete is reported to have superior physical properties compared to OPC concrete, including improved strength, permeability, durability, and chloride resistance (Pandey et al. 2012). Geopolymers typically perform well in high-temperature and corrosive environments. EPRI is researching the use of geopolymers for refractory floors in highly corrosive boiler environments, and for stabilization of soluble waste materials. Geopolymers also reduce greenhouse gas emissions associated with portland cement production by more than 50% for every ton produced (McLellan et al. 2011). This raises the possibility of increased value of geopolymers due to carbon offsets.

The primary disadvantages of geopolymer cement are the variable nature of the mixture design and handling of the highly caustic liquid activators. For these reasons, geopolymers are more difficult to use than portland cement for applications that commonly rely on ready-mixed plants in the United States. Currently, geopolymers are more commonly used for specialty and precast applications, such as flame-retardant insulation panels, corrosion-resistant concrete, high-temperature refractory, sprayable coatings for concrete pipe protection, and precast concrete pipe, blocks, and bricks (EPRI 2015).

Commercial Vendors

Alchemy Geopolymer Services (AGS)

Ruston, LA

www.alchemygeopolymer.com/

AGS is a small start-up company that evolved from a research group at Louisiana Tech University. They primarily develop and test high-performance geopolymer concretes, in particular fly ash-based geopolymers, and provide expertise and services associated with the use of geopolymers in a variety of applications. They build relationships with other larger industrial partners that can perform large-scale installation services. AGS works exclusively with geopolymer cement/concrete products.

Quadex

North Little Rock, AR

www.quadexonline.com/index.html

Quadex manufactures cementitious products for water and wastewater infrastructure. One of their products, GeoKrete, is a geopolymer-based material used to line pipes as part of in-place rehabilitation. GeoKrete provides structural stability and corrosion resistance. The material is applied by low-pressure spraying or centrifugal spinning.

HySSIL Pty Ltd

Australia

www.hyssil.com

HySSIL is a spin-off from Australia's largest research group, the Commonwealth Scientific and Industrial Research Organization (CSIRO), that commercializes sustainable building materials based on geopolymer technology.

HySSIL produces several building materials based on aerated lightweight geopolymer concrete. Among them, two building materials could be suited for the U.S. market: a) lightweight cellular wall panels and flooring systems for residential and commercial applications; and b) lightweight cellular roof tiles (to replace cement-based concrete roof tiles).

The United States is HySSIL's primary target market for both technologies. The company believes that the proposed lightweight roof tiles can be used as a replacement material in construction for the North American housing market. HySSIL is currently in talks with a roof tile manufacturer based in California. The primary market potential for this product is replacement roof tiles for lightweight roofing systems without the need to strengthen the roof structure.

The HySSIL patented process allows the manufacturing of geopolymer roof tiles to be performed in existing concrete roof tile plants without significant capital plant modifications.

The Zeobond Group

Australia

www.zeobond.com

Zeobond was initially established as Zeobond Pty Ltd by Jannie S.J. van Deventer of the University of Melbourne, and the company still has a working relationship with the university.

Zeobond's proprietary geopolymer product is called E-Crete. E-Crete uses a combination of fly ash and slag to produce the geopolymer binder. Applications of E-Crete include cast-in-place driveways, footpaths, and slabs as well as precast wall panels. E-Crete is not currently marketed outside of Australia.

Delft Solids Solutions

Netherlands

www.solids-solutions.com

Delft Solids Solutions is a contract research company equipped with an analysis laboratory that performs materials development in the field of micro- and mesoporous materials, aiming at zeolites in particular (see Section 6). The company is a spin-off from Delft University in the Netherlands.

The company proposes to make geopolymers with fly ash to stabilize existing weak and spongy soils in natural areas, for creating natural-looking cycling paths and walking trails. Delft believes the geopolymer paths/trails can be made to blend in more with natural surroundings than concrete or asphalt.

Market Readiness

Geopolymer cements/concretes are well understood from a technical perspective and are therefore considered a relatively mature technology. There is a relatively small but growing market in the United States and worldwide. Primary uses in the United States are precast products and retrofit liners for repair of sewage pipes.

Commercialization has been slow despite the large amount of ongoing research and literature related to geopolymers. In the United States this may be largely related to the predominance of the ready mixed infrastructure based on portland cement concrete, and to general inertia when it comes to incorporating new materials and processes. While much of the equipment used to make geopolymer concrete is similar to that used to make portland cement concrete, the process is more complicated and requires the storage and use of caustic liquids. Current research is aimed at replacing the caustic liquids with dry powders, and standardizing the geopolymer formulations, with the goal of making geopolymer cement/concrete more acceptable to the U.S. market.

There continues to be a large amount of research into geopolymers at universities in the United States and Australia.

Alternative Cements

Description

Alternative cements represent a wide range of binders that are not based solely on portland cement. In many cases these cements can utilize a higher percentage of fly ash than typical replacement levels for portland cement. These may include alkaline activated cements and potassium silicate, sodium hydroxide, and calcium aluminate based products (Ramenzianpour 2013; Mehta and Monteiro 2005). They cure through chemical reactions, hydraulic bonds, and multiple component binder systems. Alternative cements are used to partially or completely replace the portland cement in concrete products. Products such as grouts, caulks, thin-set materials (coating products), liners or lining systems, and precast blocks and sheets are common materials that may utilize specialty cements.

Most producers of alternative cement claim several advantages compared to portland cement. These include superior engineering performance of concrete made with the cement, and the ability to use higher replacement levels of fly ash and other supplemental cementitious materials than are typically used in concrete. In some cases, replacement levels of greater than 95% can be achieved. Alternative cements are often marketed as environmentally superior, usually due to energy savings and a smaller carbon footprint than portland cement. A significant barrier to widespread use of alternative cements in the United States is integration of new materials and nonstandard processes into the ready mixed concrete supply chain.

Commercial Vendors

Lafarge
Chicago, IL
www.lafarge-na.com

Lafarge utilizes specialized blends of cementitious and other construction materials that allow for more cost-effective mining and oil-well cements. A variety of potential mortar compositions may be engineered, depending on a particular application. For example, U.S. Patent 6277189 B1 defines the use of coal combustion by-products for lightweight structural materials as support members in mining applications. Cements for these applications may use 10% to about 25% by weight Class F fly ash and about 50% to about 85% by weight fluidized bed combustion (FBC) ash, and about 5% to about 30% by weight cementitious material.

VHSC Cement, LLC (Pozzoslag)
The Woodlands, TX
www.pozzoslag.com

Pozzoslag is a cementitious material made using coal fly ash that has been processed and activated for use in concrete. Pozzoslag can be used at high replacement rates for Type I portland cement, approximately 30-80%. The Pozzoslag material contains 75-82% by weight of Class F fly ash that has been improved through milling and air classification to increase the particle surface area (U.S. Patent 20140275349 A1). The company claims better performance than portland cement in concrete product for several measures, including durability, workability, and permeability.

VHSC produces Pozzosl原因 by first passing fly ash through their patented reactor system, which uses both physical processes (grinding and size classification) to refine the fly ash for a consistent end-product and chemical processes to create the cementitious material. Fly ash is used as the base material in the reactor system along with a pozzolanic catalyst, such as a zeolite, to produce a cementitious blend of material that meets Grade 120 slag strengths based on ASTM 989 testing protocols.

The patented process was introduced into operations in November of 2012. The company claims the process is environmentally friendly, generating 90% less in carbon emissions than the production of portland cement, and is cost-competitive with portland cement. Pozzosl原因 is currently used by ready-mixed concrete facilities in Texas for use in highways, state roads, building foundations, and precast concrete products.

CeraTech USA, LLC
Alexandria VA
www.ceratechinc.com

CeraTech began commercial operations in 2002. They market a line of products that utilize high volumes of fly ash and no portland cement. These include ekkomaxx, an alternative for conventional concrete, along with variations for chemical- and heat-resistant concrete, KemROK, and FireROK. The company markets these as green concretes due to the high fly ash content and lower carbon footprint, and claims they provide a more durable concrete with rapid strength gain and lower permeability.

The cement manufactured by CeraTech is comprised of about 95% fly ash and 5% proprietary activators. The CeraTech products use only Class C fly ash. The company is also testing the addition of a calcium source such as limestone prior to coal combustion in order to produce a higher-calcium fly ash from bituminous coal. The pre-combustion addition of calcium is being tested at power plants in China; this approach has met with some resistance at U.S. power plants due to concerns of possible impacts on the boiler operation.

CeraTech products have been used for commercial and industrial construction, highways and bridges, and military applications.

EMC Cement
Sweden
www.emccement.com/landing4a.htm

EMC Cement derives its name from “Energetically Modified Cement.” EMC produces a specialty cement by intergrinding portland cement with different supplementary materials—fly ash and/or slag—using high-intensity vibratory and/or stirred ball mills. This creates additional surface area by creating finer particle sizes and surface cracks, exposing additional reactive surfaces. The company’s technology was developed in 1992, and the resulting material, CemPozz, has been used in a broad range of applications including port and highway construction, commercial and industrial construction, and residential projects.

In the United States, CemPozz has also been used in both state and federal highway projects. The Texas and Pennsylvania Departments of Transportation have included CemPozz in specifications. These specifications allow 50% replacement of portland cement by weight.

Additionally, from 2004 to 2007 over two million cubic yards of concrete that utilized CemPozz was manufactured in Texas for highways, housing, shotcrete and masonry blocks. The company claims that concrete made with CemPozz is superior to ordinary portland cement (OPC) concrete, can use high levels of secondary cementitious materials, is cost-competitive with OPC concrete, and is more environmentally friendly.

CemPozz may be used to replace up to 70% of portland cement in concrete. CemPozz itself is manufactured with approximately 95% fly ash and 5% portland cement.

RECO Cement Products

Oconomowoc, WI

www.recocement.com

The name RECO is an acronym for Roman Ecological Cement Products. RECO cement is a mineral admixture that is comprised of portland cement, fly ash, and a proprietary mixture that may include ground glass and some form of limestone. RECO cement can utilize Class C and Class F ash. The formulation was designed to enhance strength, durability, impermeability, and workability of fresh concrete.

RECO cement combines 30-50% fly ash, 15-20% of the RECO proprietary binder (which is essentially a blend of an alkaline component such as calcitic lime kiln dust, a secondary alkaline component of calcium oxide and/or portland cement, and a glass component) and 25-50% portland cement. The cement has been used for producing slabs and precast concrete pieces, using ash with loss on ignition values ranging from 3% to 10%. Existing cement manufacturers can utilize the RECO binder by incorporating with the cement clinker at the ball mill stage. RECO cement has primarily found applications outside the United States, principally in India.

Ash Improvement Technology Inc. (AIT)

Towson, MD

www.aitcleancem.com

AIT has developed a technology/method to alter a Class F fly ash into a cementitious material. This is achieved by adding calcium oxide, silicon oxide, and aluminum oxide in various proportions, depending on the boiler design and feed coal chemistry, directly to the combustion chamber, at approximately 10% by weight of the coal. The collected ash will then have a chemistry and reactivity similar to a Class C fly ash, but with elevated percentages of calcium oxide, silicon oxide, and aluminum oxide. AIT refers to the technology as CleanCem. The combustion additive may be comprised of a variety of materials, such as limestone, ground granulated blast furnace slag, crushed concrete, crushed glass, kaolin, and silica fume (U.S. Patent 8741054 B2). The CleanCem ash product may be used to replace portland cement in concrete from approximately 25% to 95% by weight.

CleanCem is not currently being produced commercially.

Market Readiness

There are many alternative cements that use fly ash; they range from research level to mature technologies. As a whole, they can use a wide variety of coal ash types, often blended with other additives at proprietary ratios to achieve the performance goals for the manufactured material. Individual cements, however, may be limited to a specific ash type for best performance. Specialty cements have been employed for many years, and formulations are often enhanced to meet current market needs.

The market for some alternative cements is somewhat constrained by the established ready mixed industry in the United States (Slag Cement Association 2016). Because alternative cements represent non-standard materials and processing compared to portland cement, they may be difficult to use for cast-in-place concretes. Like geopolymers, alternative cements are more often used for precast and specialty products.

4

FILLERS, EXTENDERS, AND TOUGHENERS

The market for fillers, extenders, and toughening agents is large, with an estimated value approaching \$10 billion. Common mineral fillers include ground and precipitated calcium carbonate, talc, mica, kaolinite, natural and synthetic glass, feldspar, wollastinite, and titanium dioxide (rutile), to name a few. Generally, fillers are classified by shape, such as rod-like (wollastinite, ground fiberglass), round (calcium carbonate, feldspar), or platy (talc, mica). Fly ash competes in the same market as calcium carbonate. Plastics are the largest user of fillers, where they play an important role in controlling shrinkage and contributing to strength while reducing costs. Foams and rubber products are also important users of fillers, as are coatings, paints, roofing shingles, siding, and synthetic wood. Fly ash has also been researched for use in a variety of metal composites and polymer composites.

The use of fly ash as a plastic filler, paint filler, or toughening agent has a long history (EPRI 1990). The volume of material and size of the actual market is hard to judge, as it is generally marketed under brand names, such as Boral's Celceram, produced in Georgia (www.boralna.com/flyash/flyash.asp), Plasfill, produced by Ash Resources in South Africa (www.ashresources.co.za), or Sphere One's Extendospheres, produced in Chattanooga, Tennessee (www.sphereone.net), often with no reference to use of fly ash as an ingredient.

Cenospheres and Ultra-Fine Fly Ash

Description

Fly ash-derived materials in this category fall into two general types, ultra-lite (cenospheres) and ultra-small.

Cenospheres are hollow spheres with overall densities of less than 1.0, meaning they float. They are generally collected from ponds by drawing them into thick mats and skimming them off the top of the pond. They are, pound for pound, the single most valuable coal combustion product. They are critical components in a long list of applications, including low-density oil field cements, steel and iron casting, insulations, and syntactic foam. Cenospheres make up only a small percentage of the total fly ash (approximately 2%). As ponds are replaced by landfills, cenospheres will become harder and costlier to collect. Dry separation requires some combination of air classification and mechanical sieving, and has not been performed on a commercial basis.

For ultra-small filler applications, fly ash must be beneficiated to eliminate or improve some of its undesirable characteristics. Fillers need to have a very fine average particle size, generally in the range of a d₅₀ (median diameter) of 5 microns or less, and have a very tight size distribution with little or no plus-size tail. Even small amounts of coarse ash can have a negative effect, particularly on the tensile properties of a composite. The carbon must be very low or essentially zero, as carbon particles provide a very strong coloring effect, which is difficult to mask. In general, fly ash is used in applications where color is not critical.

Beneficiation options include air classification involving multiple passes, and hydraulic classification. This may be combined with combustion or roasting to remove the carbon. The generally high value and pricing associated with these materials support higher levels of processing.

Properly beneficiated fly ash has many advantages when used as a filler or toughening agent:

- An almost perfect aspect ratio (length to width of ~1). This results in a uniform composite product with isotropic properties.
- Enhanced rheological properties. Because fly ash has a smooth surface, it is easier to compound, with low air entrainment compared to platy fillers.
- Reactive silicate surfaces. Fly ash readily accepts silanes, which are molecules that react with a mineral surface and have functional groups that react with the polymer. This results in a continuous molecular bond among the components of the composite.
- A very low surface area to volume ratio. The smooth surface and aspect ratio of ~1 results in the lowest consumption of silane per unit volume of any silicate filler.

Fly ash-derived fillers can also be combined with other fillers to modify composite properties. For example, platy fillers like milled mica can increase the overall strength of a composite, but often result in anisotropic distribution of strength, which can be reduced by the use of a fly ash filler. As in the case of concrete, fly ash fillers can produce a composite melt with improved flow properties for injection molding applications. Also, the smooth surface of the fly ash filler does not provide sites to initiate undesirable cross-linking during crystallization.

Commercial Vendors

Boral Materials Technology

<http://boralamerica.com/fly-ash>

San Antonio, TX

Boral Materials is probably the national leader in the production of fly ash-derived fillers. Although the primary emphasis for Micron³ (an ultra-fine refined pozzolan) is in concrete, it is also used in polymer applications. The Celceram product, which is a “cellular ceramic material” composed of aluminosilicate glass spheres, is sold in a functionalized form for use in a number of applications including urethane, PVC, polyolefin, and latex chemistries. It is an ingredient in a host of products such as carpet backing.

Boral Materials has developed many products that use fly ash fillers and high-performance concretes. In 2016, Boral Materials opened a new U.S. Innovation Factory (www.boralamerica.com/TruExterior/About/truexterior-news/boral-unveils-industry-shaping-u-s-innovation-factory). The center will work in the areas of material science, polymer chemistry, composite products, durability testing, and process development.

Ash Resources Ltd
South Africa
ashresources.co.za

Ash Resources Ltd of South Africa is a Lafarge-controlled company that internationally markets an extended line of products derived from fly ash. They produce highly classified fly ash for filler applications discussed above. In addition, they market the Plasfill line of products for plastic, resin, and rubber applications.

Sphere One
Chattanooga, TN
www.sphereone.net

Sphere One is one of the largest of the companies in the United States that recovers, processes, and sells cenospheres. They market their materials under the Extendspheres trade name. Sphere One offers a total of eleven different grades of materials and lists 24 different applications including coatings, paints, putties, refractories, insulation, and explosives. The products are marketed through Sphere One's affiliate, the Kish Company.

Market Readiness

Fly ash-derived fillers have been used for a long time and have been involved in many applications. Because they command high prices, they can be shipped great distances and are therefore less subject to local market conditions. They do require specialized processing, and the market size for these materials is much less than for conventional concrete applications. However, fly ash-derived specialty fillers can play a major role in generating revenue and there is potential for expansion of the current market, although the total market is somewhat limited.

Metal Matrix Composites

Description

Fly ash has also been used as a filler in metal matrix composites (MMCs). MMCs are combinations of two or more materials, at least one of which is a metal. MMCs allow the use of lighter-weight materials, such as aluminum and magnesium, in place of iron and steel. Fly ash is used in the MMC to increase the hardness and the abrasion resistance of the lighter-weight materials. In addition, fly ash composites are significantly lower in cost than aluminum-silicon carbon composites (Ramme and Tharaniyil, 1999).

EPRI (1994) researched the dispersion of fly ash into an aluminum MMC (called Ashalloy), to produce a composite with greater abrasion and wear resistance. These composites contained up to 50% ash by volume. They were cast in a variety of shapes for various potential applications primarily associated with the automotive industry, including pistons and connecting rods. Automobiles are a target market due to the need for lightweight materials that are hard and resistant to wear. The research was then extended to adding fly ash cenospheres to lead to decrease the weight of lead-acid batteries (EPRI 1999).

Research has continued on the use of fly ash in metal matrix composites, in particular aluminum MMCs (Moutsatsou et al. 2009; Kulkarni et al. 2014; Hrairi et al. 2009). However, it appears that there has been limited or no commercialization of these products in the United States.

Commercial Vendors

Cyco-Systems Corporation Pty Ltd
Australia
www.ultalite.com

Cyco-Systems has developed and markets a product called Ultalite, a lightweight aluminum metal matrix composite containing between 15% and 60% fly ash. Ultalite is used in a variety of automotive parts, including brake drums and discs, engine blocks, cylinders, and pistons. The company indicates that advantages of the products include light weight, wear resistance, good machinability, and lower cost.

Ultalite was developed in the 1990s and commercialized in the early 2000s. Research has continued since that time on product improvement in association with Melbourne University and the Australian Research Council.

Intelligent Composites, LLC
Milwaukee, WI
www.intelligentcomposites.com

Intelligent Composites, LLC is an advanced materials and manufacturing company that is an outgrowth of research at the University of Wisconsin-Milwaukee. The company has developed a new metal matrix composite material, aluminum graphite silicon carbide. This material is wear-resistant, stronger, stiffer, and self-lubricating when compared to traditional aluminum alloys. Over 25 transportation components have been identified that become more lightweight and energy-efficient when redesigned with this new composite material.

Intelligent Composites is interested in developing the use of fly ash MMCs for manufacturing cylinder liners for internal combustion engines designed to reduce fuel consumption. Current combustion engine cylinders are designed with silicon carbide, which is expensive. Their objective is to replace silicon carbide with fly ash in the composite system.

The Intelligent Composites product is proposed at the research stage and is not commercialized.

Market Readiness

Fly ash MMCs have been researched for more than two decades, suggesting a mature technology. However, there appears to be little commercialization. The Australian company Cyco-Systems is active in this area in Australia and China, but there appears to be little commercialization in the United States.

Polymer Composites - Fire Retardants and Acoustic Barriers

Description

Organic foams such as expanded polyurethanes and polystyrenes have some of the best insulation values, per pound or per volume, of any competing materials. The ability to spray urethanes makes them even more flexible and valuable. The major drawback for these materials is their high flammability. In addition, polymer composites can release toxic gases when they are burning. The flammability has been addressed by adding flame retarders, which have typically been based on halogenated organic compounds. Because the environmental safety of these compounds has been brought into question, there is interest in the use of other kinds of retardants based on inorganic additives including aluminum trihydrate and fly ash.

Using fly ash as a flame retardant is still in the infancy stages of research. For example, inorganic additives such as aluminum trihydrate or fly ash, added to a two-part expanding polyurethane foam, could function as a flame retardant for the insulating material, as opposed to added halogenated organic compounds. However, carbon in the ash would be an issue, and would need to be addressed before compounding.

The mechanism for reducing the flammability is somewhat different than for the halogenated retardants. The halogenated materials form a char, which slows down oxidation, while the ash filled urethane forms an inorganic crust, which helps to retard combustion.

Research Organizations

University of Kentucky Center for Applied Energy Research
Lexington, KY
www.caer.uky.edu

The University of Kentucky Center for Applied Energy Research has been conducting research on fly ash-based, nonhalogenated flame retardants since 2010, and has had good success (Oberlink et al. 2015). Their research was based on using ash from multiple sources, with minimal beneficiation. It was found that their ash-based flame retardants not only improved the overall strength of the polyurethane foam, but was able to successfully pass the FMVSS 302 – Flammability of Materials Used in the Interior of Motor Vehicle Occupant Compartments Test.

The UK CAER flame retardant project is currently in the pilot-scale phase.

National Institute of Clean-and-Low-Carbon Energy
China
www.nicenergy.com/en/

The National Institute of Clean-and-Low-Carbon Energy, or NICE, is a company that is part of the Shenhua Group, based in Beijing, China. Their primary objective is to research and develop fly ash-based core material technology and products. One current focus is the development of nonhalogenated flame retardants, which is classified as their NFR product series (Zhao et al. 2015).

NICE's NFR product series is currently in the pilot-scale production phase.

North Carolina Agricultural and Technical State University (NCA&T)
Greensboro, NC
www.ncat.edu

Dr. Kunigal Shivakumar at NCA&T has been researching the use of fly ash as a filler in polymer composites for several years. He developed Eco-Core, a structural material for navy ship hulls that provided superior fire resistance and toxicity control. The material used cenospheres for lightweight ships. Eco-Core was successfully developed but is not yet commercialized.

Dr. Shivakumar is now researching the use of a wide range of ash types for producing polyurethane matrix composites that contain up to 80% fly ash for both short- and long-term applications. The short-term applications include reusable ash storage blocks that greatly reduce leaching of heavy metals. The longer-term applications include manufacturing of broad range of building and infrastructure products that include fire resistant roofing, siding, decking, railway ties, and utility poles. Research on these products is in the early stages. Dr. Shivakumar has successfully tested fly ash from bituminous coal-fired power plants in this process, as well as ponded and beneficiated ash.

This technology is at the R&D stage and has not yet been commercialized.

Carbon Air Limited
United Kingdom
<http://carbonair.eu>

Carbon Air Limited is a spin-off company from the University of Salford Acoustic Research Group with expertise in the development of high-performance acoustic materials. This company is researching the use of fly ash in acoustic absorbers in applications such as noise barriers for motorways, trains, and other transport and industrial infrastructure projects.

Market Readiness

Polymer composite products are at the research stage, and not yet commercial. Research has been promising and is expected to continue to advance toward commercial applications. Further development in this area may accelerate if the current generation of flame retardants is banned or restricted.

5

METALS EXTRACTION

Commercial mineral extraction from coals has been available since the 1800s, when a number of plants operated in the United States for recovery of vanadium and silver from coal mines. Currently, the interest in extraction from coal ash has increased due to environmental concerns and resource issues related to mining raw materials, and the risk of supply shortages for certain critical materials. Despite the growing interest in this technology there remains uncertainty about the regulatory and economic aspects, as well as a lack of data on the full environmental footprint of the various metal recovery processes.

The value of metal content within fly ash depends upon the concentrations of elements, which can vary considerably depending on the source of coal burned (Tolhurst 2015; Matjie et al. 2005; Bai et al. 2011; Yao et al. 2014; Lokeshappa 2012). This fact alone makes it somewhat difficult to accurately assess the potential of this technology as a broad-based approach to utilizing ash.

Aluminum, Magnesium, and Other Metals

Description

Alumina can be recovered by a low-temperature hydrometallurgical process utilizing a chloride leach solution or by acid-leaching at high temperature using hydrochloric acid (Bai et al. 2011; Yao et al. 2014). All the metals (except titanium, but including rare earth elements) dissolve as chlorides. Specifically, alumina and iron dissolve to form aluminum chloride (AlCl_3) and ferric chloride (FeCl_3). Silica and titanium remain insoluble and are removed by filtering. The leachate is processed by first precipitating the aluminum chloride and removing it as aluminum chloride hexahydrate (ACH), the precursor of alumina. The ACH then goes through calcination and is transformed into alumina. The ferric chloride, which is still in the leachate, is hydrolyzed, using a low-temperature process, producing pure ferric oxide precipitate while regenerating hydrochloric acid. The ferric oxide (hematite) is very pure and can be sold commercially as a specialty by-product. The low-temperature process produces a filter cake, in addition to the alumina, which is a product marketed as Micro Silica and has been used in the cement industry for the production of high-strength concretes. Fly ash currently being used for aluminum extraction in China has a very high alumina content, in the range of 30-35% by weight.

Magnesium has the highest strength-to-weight ratio of all common structural metals and is increasingly used in the manufacture of car parts, laptop computers, mobile phones, and power tools. Magnesium is typically extracted from ash with mild hydrochloric or nitric acid. Gold may also be extracted from fly ash using the chloride-based extraction technology.

A significant concern with all metals extraction technologies is the volume and character of wastes produced by the process.

Commercial Vendors

Latrobe Magnesium
Australia
latrobemagnesium.com

Latrobe Magnesium is in the process of building a magnesium plant in Victoria's Latrobe Valley, with plans to use a hydromet process combined with the thermal reduction process. The plant will extract magnesium from industrial fly ash, the by-product of local brown coal power plants. A feasibility study was successfully completed, and a study is currently under way to justify this process commercially. The company states it will initially produce approximately 5,000 tons of magnesium metal per year.

Three of Victoria's power generation plants reside in the area of the magnesium plant, with the valley containing a 25-million-ton inventory of fly ash. An additional 500,000 tons of ash is added annually. Currently Latrobe plans to sell the refined product under long-term contracts to Australian and American users. The company plans to expand the plant, allowing it to further penetrate the annual global market of more than 800,000 tons.

Elixsys
Clarksville, VA
<http://www.elixsys.net>

Elixsys is licensed by Eagle Harbor Holdings to market the intellectual property of its two base patents for extraction of metals from various waste streams including fly ash. The technology was originally developed to treat electric arc furnace dust, a by-product from the production of steel.

The Elixsys technology utilizes a low-temperature hydrometallurgical process coupled with a chloride leach solution to recover metals from fly ash. The process removes all nonferrous metals such as lead, titanium, copper, and nickel from fly ash in the form of metal chloride. The technology utilizes a zinc cementation process to recover metals present in the ash. While this process is popular due to its relatively simple operation and low energy demand, the drawback is the large amount of spent leaching solution that now contains solid residue that must be washed and stabilized before final disposal. The company would like to market the remaining solids (filter cake without metals) as Micro Silica for use in concrete and ceramics.

Elixsys is not currently working with any fly ash from power generation plants, but the company's technology is designed specifically to work with fly ash. They are currently working with cogeneration plants (rock burners) in Pennsylvania. The company states that the processing creates no new waste streams.

Orbite Technologies Inc.
Montreal, Canada
<http://www.orbitetech.com/English/Home/default.aspx>

Orbite Technologies Inc. has developed the patented Orbite process, an acid extraction used to produce alumina and magnesium from fly ash and other materials. The Orbite process consists of four main steps: aluminum ore prep, leaching, extraction of alumina and iron, and calcination.

The selective extraction process can also be used to process a wide range of other metals, including scandium, gallium, and rare earth metals. The company has plans to commercialize the process in the United States.

Orbite is currently converting their high-purity alumina (HPA) extraction plant (located in Cap-Chat Quebec) for multi-feedstock utilization, which will allow for the extraction of gold by 2017. Using Orbite's multi-feedstock technology, they estimate the average value for typical fly ash is around \$200 - \$250 per ton. Even at an average concentration of 7.5 ppm of gold in fly ash, a 50% recovery would increase this value to \$350 - \$400 per ton.

Industrial Gasification LLC

Industrial Gasification, LLC is a start-up engineering company aiming at further developing and commercializing the fluidized catalytic gasification (FCG) technology. They are partnering with the Institute of Combustion Science and Environmental Technology (ICSET) at Western Kentucky University.

The FCG process was developed for generating syngas and removing contaminants from coal, petroleum coke, and biomass feedstocks. R&D activities successfully demonstrated the technology viability for removing contaminants from coal, but no commercial units have been built. Laboratory, bench-scale, and pilot-plant operations were conducted in the 1970s. Intellectual property consisted of more than 30 patents (now in the public domain) and proprietary developments that covered the FCG catalyst, gasification operating system, catalyst preparation and purification unit, and other innovations.

This technology can be used to remove metals from fly ash because heavy metals such as iron, nickel, and vanadium gravitate to the base of the gasification reactor for removal as metal concentrates. The lighter silica and aluminum oxide compounds of the coal ash float on top of the operating catalyst and are withdrawn as an improved quality product.

Industrial Gasification is planning an independent evaluation of the FCG catalyst and process in an effort to re-establish the technology. This will be completed at the ICSET research facilities.

This is considered an early research phase process that will require significant development prior to commercialization.

Market Readiness

The main current commercially scaled-up activity for the recovery of metals from coal ash is for germanium in China and Russia. These areas have enriched coal seams and are processed to recover the metals from the ashes. There are also some commercialized processes for extracting aluminum in China, such as the Datang International Power Generation Company in Tuoketuo (Yao et al. 2014). This particular plant went into operation in 2012 and is aiming to produce 500,000 tons of alumina and 560,000 tons of active calcium silicate. The Shenhua Group in Erdos is aiming to produce 4 million tons of alumina annually. Studies have shown that for coals with enriched levels of aluminum, a return of \$210 to \$245 per ton of fly ash may be seen with current (2015) market prices. Several U.S.-based companies have commercial technologies for the digestive processing of fly ash for the extraction of metals; however, there are no companies in the United States that have scaled up for commercial production.

Rare Earth Elements

Description

The rare earth elements (REEs) on the periodic table are the 15 lanthanides (lanthanum [La], cerium [Ce], praseodymium [Pr], neodymium [Nd], promethium [Pm], samarium [Sm], europium [Eu], gadolinium [Gd], terbium [Tb], dysprosium [Dy], holmium [Ho], erbium [Er], thulium [Tm], ytterbium [Yb], and lutetium [Lu]). Yttrium [Y] and scandium [Sc] are also often grouped in with the rare earth elements, due to their chemical similarities with the lanthanides (NRECA 2013).

Due to the high demand for many REEs, coal combustion fly ash represents a potential and readily available source from which to extract rare earth elements. The concept of recovery of REEs from fly ash has been around for a very long time, and has recently gained in popularity due to the global demand for REEs in electronics and automobiles, as well as their use in some of the United States' defense applications. Rare earth elements are used in a variety of common devices such as computer memory, DVDs, mobile phones, hybrid cars, and rechargeable batteries (<http://geology.com/articles/rare-earth-elements/>).

In 2015, rare earths were mined for part of the year by one company in the United States—Molycorp Inc., in Mountain Pass, California. Molycorp ceased operations in October of 2015 following a dramatic global drop in prices due to new supplies from mines in China and the development of REE alternatives (<http://investorintel.com/technology-metals-press/a-rare-earths-economics-lesson/>).

The United States continues to be a large importer of rare earths, importing upward of \$150 million dollars' worth in 2015, which is a decrease from the \$191 million dollars' worth of rare earths imported in 2014 (USGS 2016). The current market for rare earth elements in the United States breaks down as 60% - catalysts, 10% - metallurgical applications and alloys, 10% - ceramics and glass, 10% - glass polishing, and 10% - other.

Research Organizations

Department of Energy National Energy Technology Laboratory (DOE-NETL)
Pittsburgh, PA

<http://energy.gov/fe/articles/doe-selects-projects-enhance-its-research-recovery-rare-earth-elements-coal-and-coal>

The DOE National Energy and Technology Laboratory is currently sponsoring a major research initiative on the recovery of rare earths from coal and coal by-products including fly ash. In Phase 1, they are funding 10 projects for possible bench-scale and pilot-scale testing. Phase 1 will include 1) characterizing coal and CCP samples for potential recovery of REEs; 2) performing technical and economic feasibility studies; and 3) developing an initial system design. They plan to select four projects to advance to bench-scale and pilot-scale testing in Phase 2, based on the Phase 1 results. The 10 Phase 1 projects are listed in Table 5-1.

Table 5-1
DOE research projects funded to assess recovery of rare earth elements from fly ash and related materials

University of Wyoming (Bench Scale)	Three-step extraction process using carbon dioxide and ferric chloride under supercritical conditions for Powder River Basin coal ash
Duke University (Bench Scale)	Solvent extraction and membrane filtration on a range of CCP types
West Virginia University Research Center (Bench Scale)	Two extraction processes for recovery of REEs from acid mine drainage (AMD) and AMD sludge
Neumann Systems Group (Bench Scale)	Extraction using supercritical carbon dioxide/cosolvent and conventional acid/base extraction for subbituminous, bituminous, and anthracite ash
Battelle Memorial Institute (Bench Scale)	Closed-loop acid digestion for Ohio coal and coal ash
University of North Dakota (Bench Scale)	Chemical treatment and REE separation from North Dakota lignite, coal sediments, and coal drying refuse
University of Kentucky Research Foundation (Pilot Scale)	Physical and chemical separation methods for Central Appalachian bituminous coal preparation plant refuse
Physical Sciences, Inc (Pilot Scale)	Physical/chemical separation for coal ash from burning Eastern Kentucky fire clay and anthracite refuse
Southern Research Institute (Pilot Scale)	Plasma-based recovery from Central Appalachian, East Kentucky bituminous coal ash
Tusaar, Inc. (Pilot Scale)	Extraction and metal sorption media for ash from Kentucky and Ohio power plants

Mitton Cavitation

Canada

www.mittoncavitation.com

Mitton Cavitation is a privately owned company that was incorporated in 2004 in Brantford, Ontario, Canada. The company licenses applications of its proprietary low-energy, high-volume hybrid hydrodynamic-acoustic cavitation reactor system.

Cavitation is essentially the breaking down of emulsions—a particle or droplet that is suspended in an aqueous medium. In order to break a stable emulsion, it is necessary to break or change the electron charge that is surrounding the particle. Cavitation causes the creation and collapse of microbubbles, which changes the electron charge surrounding the particles suspended in water, and breaks the emulsion. The breaking of the emulsion results in stratification—the falling of the particles out of water. The stratification of the particles results in the ability to remove particular materials from water.

The use of different inert gases, as well as the use of different chemical additives to mitigate chemical oxygen demand and pH effects, facilitates the manipulation of the process and results in layered stratification of different materials. This allows for the selective removal of certain elements. Although they have not specifically done work on REE recovery, Mitton Cavitation believes that using the same technology and general procedures they used for metal removal would be an easy adjustment to begin working in the REE recovery field, as they already have the technology to separate and remove metals from other materials.

Periodic Products

Fort Lauderdale, FL

<http://www.periodicproducts.com/>

Periodic Products is a company that was founded in 2009 by Dr. Joseph P. Laurino in Fort Lauderdale, Florida. They have developed, patented, and manufactured nontoxic polymers that bind heavy metals and rare earth elements through the combination of ion exchange technology and adsorption. The targeted soil is treated with an aqueous solution. That aqueous solution is then treated with Periodic Products' patented polymers, which will bind and adsorb the REEs out of solution.

By using a resin with proprietary nontoxic polymer adsorbents, the Periodic Products ion exchange process is able to adsorb materials by their specificity—their resins do not bind calcium or sodium, allowing for their use in hard water and salt water environments. The binding capacity of their resins is 100 times greater than that of typical ion exchange resins, and they have a very rapid rate of adsorption.

Currently, the Periodic Products technology is commercialized in several non-coal ash related industries, and has recently been investigated as a possible solution to both production yield issues and hazardous waste concerns in the mining and energy production markets. In a study that was cofunded by the Florida Industrial and Phosphate Research Institute, the Periodic Product proprietary extraction and isolation technology was successfully applied to rare earth elements and radionuclides from the three major waste products associated with the production of phosphate fertilizer. They have also successfully conducted bench-scale studies with fly ash of various qualities for REE recovery.

Periodic Products prototype technology has been completed, and the company is currently in the design and build phase of their mobile pilot-scale units for REE recovery from phosphorus waste. Scale-up of production to the size required for most applications is estimated to cost \$500,000 - \$2,000,000.

Orbite Technologies Inc.

Montreal, Canada

<http://www.orbitetech.com/English/Home/default.aspx>

See Metals Extraction.

UCORE
Bokan Mountain, AK
mrt.ucore.com

UCORE is a self-described “junior” mining company that has extensive experience working with REE ores. The company has spent considerable effort in the development of REE recovery from the Alaskan Bokan-Dotson Ridge uranium mine. UCORE expertise is in the field of separation of REE elements using molecular recognition technology (MRT) from concentrates, including concentrates potentially derived from fly ash processing. These concentrate solutions are obtained through washing the REEs that are bound on the UCORE SuperLig column with an acid. MRT was originally developed by IBC Advanced Technology (<http://www.ibcmrt.com/>); IBC specialized in ligand technology for separation and isolation of precious metals from solutions.

UCORE is currently completing a pilot facility for separation of REE, which is slated to open in Spring 2016, using MRT technology. The company claims that the technology is able to recover high-purity REE from low concentrations in ash in an environmentally friendly manner, as it minimizes waste generation.

Market Readiness

Recovery of REEs from fly ash is not yet a commercial process. However, many companies and universities in the United States have been engaged in research and development over the last decade due to the REE supply shortage and price increase in about 2010. It is unlikely that a commercially viable process will emerge in the near term under the current supply and demand conditions. However, as evidenced by the market volatility over the last decade, market conditions can change rapidly for this commodity.

6

OTHER PRODUCTS AND TECHNOLOGIES

Proppants

Description

Proppants are used in the production of shale gas and oil as recovered by fracking technology. Proppants are sand or sand-sized particles used to stabilize the production wells and hold fractures open and are critical in maintaining flow and recovery of oil and gas. They represent the bulk of the cost in developing a producing well via fracking and represent a sizeable industry. It is estimated that about 45 million tons of proppants were used in 2013

(<http://www.marketsandmarkets.com/Market-Reports/proppant-market-802.html>).

Total product valuations were estimated to be about \$7 billion in 2013. Although difficult pricing issues in oil and gas have resulted in a slowdown in shale gas and oil production, two trends were evident over the past few years. The first is the trend of increasing proppant tonnages per well. The second trend is the use of materials with finer particle sizes. The impact of these trends is increased production and longevity.

Proppants need to be strong and uniform in size to produce a porous, permeable, and stable pack. Low density is also a desirable property. There are several different kinds of materials used for proppant production. The largest by volume are natural quartz sands as mined in the Midwest (Wisconsin and Illinois). Screening and washing is used to produce uniform sizes. U.S. Silica is a major producer in this segment of the market. Synthetic proppants are formed by firing aluminosilicates to produce exceptionally strong, well-rounded pellets. Although synthetic proppants are more expensive than the natural materials, their strength makes them useful at greater depths and pressures. Their generally lower density also provides an advantage. These materials may also be resin coated to further lower density and improve buoyancy.

The use of fly ash in proppants has a long history and is referenced in almost 150 U.S. patents. Most of these refer to the use of fly ash as a potential ingredient in the fabrication of synthetic proppants.

Commercial Vendors

Ecopropp Pty Ltd.

Australia

<http://imformed.com/proppant-promise-from-australian-fly-ash/>

This start-up Australia-based company was recently acquired by Coretrack Ltd., based in Perth Australia. Coretrack is an oil and gas technology company. Ecopropp has developed a process to produce a synthetic proppant primarily from fly ash, with the use of bauxite as a major secondary ingredient. They use a sintering process to combine the ingredients.

Ecopropp has recently completed construction of a kiln-based pilot plant at a coal-fired power plant outside of Brisbane, Australia. The product is reported to be in the 30 to 40 mesh size range and is purported to perform well on the ISO standards strength test, achieving an overall strength of 15,000 psi.

NuForm Materials, LLC

Lexington, KY

www.nuformmaterials.com

This Kentucky-based start-up company has been working on the development of a “micro-proppant” derived from fly ash via classification technology. The concept is to produce a proppant of exceptional permeability by extracting a very narrow particle size range from the coal ash. This material would be used in conjunction with a much coarser proppant (i.e., the gravel pack) to hold the fine fractures open. Maintaining the fine fracture structure in the shale is important in extending the life of shale-based oil and gas wells.

NuForm Materials recently completed a series of pilot-scale tests of its separation/classification technology at an active ash pond in Ohio. During the test, a concentrate of appropriately sized material (75 x 150 μm , with a $d_{50} \sim 85 \mu\text{m}$) of 25% by weight was achieved. This material, upon further processing, developed a hydraulic conductivity of 1.5×10^{-2} cm/sec. This is essentially a silt-sized material with the hydraulic conductivity of a sand. The smooth particle shape of the fly ash reduces resistance to flow compared to equivalent-size synthetic or even natural proppants. A joint patent with the University of Kentucky Research Foundation was filed in 2015, and work continues to refine the material.

Market Readiness

Fly ash proppants are in the development stage, and are not yet commercial in the United States. There is expected to be a moderate-size market when fracking operations recover from the recent commodity price drop.

Zeolites and Wastewater Treatment

Description

Zeolites are porous hydrated aluminosilicates characterized by a high surface area that allows them to act as absorbents and chemical filters, to carry specialty molecules (as in detergents), and to trap water molecules to help dry natural gas. There are more than 40 natural zeolites such as clinoptile and chabazite that can be found in areas where volcanic rocks and ash are mixed in an alkaline environment. Their major uses are as molecular sieves, commercial absorbents, and catalysts.

It takes tens of thousands of years for natural zeolites to form (EPRI, 2002). Synthetic zeolites can be synthesized in a short time period by reacting an ash material with a highly caustic sodium hydroxide solution at elevated temperatures. Synthetic zeolites have been commercially available for more than 50 years. The market for synthetic zeolites is dominated by large chemical corporations. Manufacturing of synthetic zeolites is generally customized for specific uses such as detergents, catalysts, gas drying, and water treatment.

The most important characteristic of zeolites in these applications is the high ion exchange capacity. Fly ash can be used as a precursor for manufacturing synthetic zeolites. A typical process consists of boiling the ash in a 2-3M NaOH solution for 1-3 days, often with the addition of another source of alkaline earth elements and silica, such as cement kiln dust or glass cullet (EPRI 2002). Research on the development of zeolites from fly ash has been performed at EPRI, universities, and other organizations over the past two decades. Fly ash zeolites generally compete with natural zeolites for adsorption applications in agriculture and water treatment.

Commercial Vendors

ChK Group, Inc.

Plano, TX

www.chkgroupinc.com

ChK Group is a small business focused on transferring early-stage R&D research to commercial markets. They focus on use of solid industrial wastes and nanotechnologies. ChK proposes to convert fly ash into a Type A zeolite coated with iron that can be added to sand and used as material for golf greens. The advantages of this material will be high cation exchange capacity, retention of water and nutrients, and reduction of nitrogen, phosphorus, and potassium run-off from excess fertilizing.

ChK estimates that in the future about 20 new golf courses will be added yearly in the United States, each consuming between 10,000 and 20,000 tons of fine sand. Assuming a zeolite dose rate of 5-10% to the sand, the maximum amount of fly ash-based zeolite that could be used yearly in the United States is 40,000 tons.

This technology consumes a relatively small amount of fly ash and has only been demonstrated at the laboratory scale.

Clariant

Switzerland

<http://www.clariant.com/en/Corporate>

Clariant is a large chemical manufacturing company and one of the world's largest producers of specialty zeolites and zeolite-based catalysts. They manufacture four types of zeolites, called BEA, FAU, MoR, and MFI zeolites. Clariant has investigated the potential of various grades of fly ashes as a raw material for their production, including some pilot-scale demonstrations. They have concluded that fly ash offers no benefit over the conventional silica sources for the production of their line of zeolites.

Toyo Tanso Co, Ltd.

Japan

www.toyotanso.com

Toyo Tanso manufactures isotropic molded graphite, carbon-fiber composites, and other products based on carbon. The Business Incubation Division of Toyo Tanso is considering producing pellets consisting of carbon powder and fly ash in a polymer matrix. These pellets will be designed for the recovery of phosphate from wastewater. The quantity of phosphorus in wastewater in Japan is approximately 55,000 tons/year.

Research Organizations

Consejo Superior de Investigaciones Científicas (CSIC) Spain

The CSIC in Barcelona, Spain, has been performing research on fly ash-based zeolites for many years. Several types of processes to produce zeolites from fly ash have been thoroughly investigated. A brief summary of the research results follows.

Fly ash-based sodium zeolites. CSIC has partnered with a large chemical manufacturer of synthetic zeolites (Clariant) to produce sodium-based zeolites (called NAPI). They used a test reactor to produce four tons of NAPI with a cation exchange capacity (CEC) of 3.5 meq/gr in 8 hours. The results were good, but marketing this product in Spain was challenging, and the only use that was possible was mine reclamation. This technology is at the pilot demonstration stage.

Fly ash-based potassium zeolites. CSIC has developed a process to produce potassium zeolites using fly ash as a precursor in a laboratory-scale production with a 10-m³ reactor. They subsequently mixed the potassium-zeolites with nitrates to produce a fertilizer, which they believe could have a good market for commercialization. CSIC has investigated the ability of this process to handle ashes with different compositions. The Si/Al ratio and the glassy or mullite content of the fly ash are very important in determining the outcome of the process. CSIC developed special recipes according to the characteristics of each batch of fly ash. This technology is at the laboratory-scale stage.

Synthetic zeolites based on extracting Al and Si from fly ash. CSIC has also tested a process of extracting aluminum and silica from fly ash to produce a concentrated lixiviate that is used to manufacture a high-quality zeolite. The process is very costly and generates a lot of residue, since only Al and Si are used from the fly ash. For these reasons, this process is not currently being studied.

Alkaline Fusion. CSIC has tested a process combining sodium and fly ash at very high temperatures (~600°C) to produce a zeolite with very high reactivity at a laboratory scale. The process is costly but does not generate significant residue, because all of the fly ash is combined. Potential uses for this product are in mine reclamation and gas drying. Its use as soil amendment is not possible due to the sodium content in the zeolite. This technology is at the laboratory-scale stage.

State University of New York
Buffalo, NY
www.buffalo.edu

Professor John Atkinson proposes to manufacture porous zeolite structures based on fly ash and load them with iron to be used in water treatment applications. Potential applications may include arsenic adsorption, hexavalent chromium reduction, and dechlorination. This work is at the conceptual research stage.

University of Illinois - Chicago
Chicago, IL
www.uic.edu

Professor Amid Khodadoust proposes to use coal ash to remove heavy metals and organic microorganisms from water. The research includes a study on the removal rates in batch and column studies using different size fractions of the ash. Additionally, removal of low concentrations of organic contaminants based on the content of iron oxide in fly ash will be assessed through batch studies. This work is at the conceptual research stage.

Market Readiness

Among all markets where natural and synthetic zeolites have been used, the ones that have seen some exploratory research for fly ash-based zeolites are mine reclamation, soil amendment, ammonia control, and gas drying. However, to the authors' knowledge, there are currently no commercially available fly ash-based zeolites in the United States.

Research in the past has proven the feasibility of producing fly ash-based zeolites, but research on process technology has been lacking. Therefore, the processes have not been sufficiently developed to be optimized and result in competitive production schemes. As a result, zeolites from fly ash are still too expensive and have not been fully developed as compared to other synthetic zeolites that offer high purity for competitive prices.

The costs associated with processing the fly ash appear to be the primary factor limiting broader market penetration. EPRI (2002) estimated that fly ash zeolites could be synthesized for \$100/ton or more. Secondly, markets for fly ash-based zeolites are not well defined, and the advantages of using this material to replace natural zeolites have not been demonstrated.

Plasma Arc/Vitrification

Description

Plasma arc gasification and vitrification is a process that converts the organic matter in the feed into synthetic gas and the inorganic materials into a vitrified (rock-like) material. The temperatures required for this process are above 2700°C, and therefore it is very energy-intensive. Note that this is not an incineration or burning process, since organic matter is decomposed through molecular dissociation. The primary purpose of vitrification is environmental, to limit the release of metals from waste materials and to decrease the volume of the waste stream.

Plasma arc vitrification systems are being used to treat ash from municipal solid waste incinerators in Japan. Local government regulations require all new municipal waste incinerators to be equipped with an ash vitrification system (Hanus and Mustoe, 2003).

The costs associated with plasma arc technologies are high. A simplified analysis, done for an ash melting equipment by assuming an estimated capital cost of \$7.5M for a 200 tons of ash per day system and assuming a nominal electricity cost of \$0.06 kWh, resulted in a total operating cost of \$100/ton of ash. This analysis includes the costs of electricity, labor, additives, capital depreciation, and maintenance and repair [for more details, refer to Hanus and Mustoe, 2003].

Commercial Vendors

Phoenix Solutions Co
Plymouth, MN
www.phoenixsolutionsco.com

Phoenix Solutions Co has been operating commercial ash vitrification systems for municipal solid waste systems in Japan for over 20 years. Of the 1200 waste incinerators operating in Japan, 110 incorporate ash-melting, with 60 utilizing electric arc plasma systems. Of the electric arc plasma systems in commercial operation, Phoenix Solutions has supplied 16 units. It is the largest supplier of such commercial equipment in Japan.

Phoenix Solutions customers in Japan utilize the vitrified ash for a variety of applications: as soil amendment, runway land extensions (especially in harbor and island configurations), and construction material reinforcement; in decorative features such as parking lot curbing, park tables and benches; and in architectural pieces such as interior and exterior tiles for walls and floors.

Phoenix Solutions proposes to utilize its 1.5-MW plasma heating system equipment at its Corporate Test Facility in Hutchinson, Minnesota, to process up to 600 pounds/hr of fly ash, converting it to glass-like material with specific engineering properties. For example, it is possible to interact the molten material with other gases to make fiberglass insulation, small beads, or hollow beads, which would allow for acoustic, thermal, or EMF attenuation. Casting for architectural purposes is also a possibility; small doses of additives used at the beginning of the process could change the color of the glassy material for aesthetic purposes.

Processing smaller feed volumes results in greater value-added potential. Phoenix Solutions can generate nanometric particles at a pilot scale. Although limited to approximately 0.5 to 1.0 tons per day in the demonstration setup, designs have been developed for production capacity of up to 10 tons/day. Particle sizes in the 50-nm range are achievable, opening the possibility of a new spectrum of fly ash-based materials that could be used for engineered thermal conductivity, specific heat, acoustic properties, and density. For example, depending on how the nanometric powder is handled (i.e., sintering it or combining it with another material), the thermal conductivity, density, and specific heat can be controlled to turn it into user-specific products.

Applied Plasma Arc Technologies, LLC
Atlanta, GA
<http://www.plasmatech.us/about-us-2/>

Applied Plasma Arc Technologies, founded in 2010, is a consulting company focused on further development of plasma arc vitrification. The company proposes to design and build a prototype plant near a coal plant to demonstrate gasification and vitrification of production and stored ash, producing construction materials such as aggregates, sand, metal nodules, or plasma wool. Commercial plasma systems have been in operation for several years to convert incinerator ash into inert rock-like sand and aggregate by-products that are sold as construction materials, mainly in Japan.

Among the high-value building materials that can be produced, plasma wool insulation is promising. Plasma wool insulation can be used as a replacement for fiberglass insulation in the residential and commercial markets. A 1000 tons/day plasma plant processing coal ash could produce 150 tons per day of plasma wool insulation. Plasma wool can also be used for stabilization of oil spills. Plasma wool insulation has been shown to be a more efficient insulation than fiberglass, and to be significantly less costly. Plasma wool can be sold for \$0.20/lb, or \$400/ton (Circeo 2010).

ArcSec Technologies, Inc.

ArcSec Technologies, Inc. was founded four years ago and has a technical group based in Connecticut and Alabama. Their technology is based on molecular thermal depolymerization and reformation by the use of an arc plasma. The arc plasma is used to reach temperatures above the Gibbs free energy to depolymerize the materials without the introduction of combustion air. By controlling the reaction temperatures (and the chemistry in the furnace), it is possible for the technology to recover trace metals, and additionally recover energy that may be otherwise lost. The use of a graphite electrode to create a plasma is very well known to, and used in, the steel industry. The equipment used is a variation of the electric arc furnaces used by the steel industry and has a similar cost.

The use of a thermal plasma on the ash converts the ash into a basalt-like material, which can then be used for aggregate or other applications. The molten slag can also be turned into fibers and converted into rock wool, which has multiple uses, such as for insulation

ArcSec Technologies believes that the best application of their technology would be to install an oversized furnace, capable of processing a full day's ash production overnight, next to a coal-fired power plant. They would have the system operate only at night when the power demand is reduced, and allow the furnace to be banked and remain at temperature during the day when power demand by the grid is high. In that manner, the technology could be used to convert the ash into inert materials, recover metals, and possibly convert the ash into fiber.

EOSMYCO, Inc.

Charlotte, NC

www.eosmyco.com

EOSMYCO is an environmental research facility that evolved in 2013 from research on nanotechnology at the University of North Carolina at Charlotte. Although they were primarily concerned with bioremediation processes and mining, they partnered with Areva Federal Service LLC to evaluate feasibility of a vitrification process to remediate and use coal ash resources in North Carolina. Areva has developed a vitrification process that utilizes a cold crucible induction furnace. The goal of the process was to first vitrify the ash, and then create aggregate from the glass product.

The EOSMYCOS project was discontinued after market analysis suggested that it was not economic. The vitrification process cost more than ten times the value of aggregate in North Carolina. Areva continues to explore the process with possible application for rare earth element recovery. ECOMYOS indicates that any development of this technology is at least three to five years away.

Market Readiness

Vitrification systems are commercially available and are currently being used to treat municipal solid waste ash in Japan on a continuous commercial basis. However, none of these systems are currently working for the application of vitrifying coal ash. For fly ash, the technology is still at the early commercial development stage, not pilot-scale level. There are some vendors that are offering commercial systems for coal ash, but they have not been demonstrated to be technically and economically feasible at power plant scale.

The traditional ash vitrification system that results in the production of glassy aggregates that can be sold in the construction industry does not appear as a robust economic alternative for ash utilization. However, the system proposed by some vendors to produce high-value materials, such as rock wool type insulation material (by spinning the vitrified ash) or to recover REEs, could potentially see a viable market given the higher price.

Wastewater Brine Stabilization/Solidification

Description

New effluent guideline regulations require power companies to treat wastewaters from flue gas desulfurization (FGD) systems. The goal is to eliminate wastewater discharges. Power companies are considering a wide range of treatment options, including zero discharge systems and wastewater volume reduction. These processes result in concentrated wastewater brines that require disposal. One management option is mixing with CCPs and possibly other reagents to stabilize/solidify the brines and disposing of the resulting solid in a landfill. The success of this technology depends on encapsulation of the brine and long-term stability in the landfill environment.

This technology can potentially use large volumes of CCPs to provide the dual benefit of ash use and wastewater residuals management. Ideally, both the wastewater and the CCPs will be stabilized to reduce salt and trace element dissolution that might otherwise occur, with ultimate disposal in an engineered landfill. This technology is already available in the industry to stabilize scrubber sludge and more dilute wastewaters.

Research Organizations

Electric Power Research Institute (EPRI)
Palo Alto, CA
www.epri.com

EPRI has initiated a large, coordinated research effort to evaluate holistic solutions, including technologies for wastewater treatment, stabilization/solidification of the brines and residues, and disposal in landfills. Evaluations in this project will incorporate mixing methods and materials, chemical properties of ingredients and final products, and physical properties of final products. The research will consider various concentrations of wastewater, solid materials, and reagents to provide insights into chemical reactions and resulting physical properties important for landfill applications. This research is expected to provide viable alternatives within two to three years.

Market Readiness

This technology is at the research stage. However, the current industry need suggests that research by EPRI and commercial enterprises will be accelerated to provide viable technologies within a timeframe of a few years.

Asphalt

Description

Fly ash can be used as mineral filler in the production of hot-mix asphaltic concrete. The fly ash is used to replace some of the asphalt binder, similar to the replacement of portland cement in concrete, and possibly in lieu of polymers added to improve asphalt qualities. The fly ash can extend the oil binder and improve asphalt durability and performance compared to polymer addition (Sobolev et al. 2013; Tapkin 2008).

Asphalt binder comprises 5% of the asphaltic concrete mix; the remaining 95% is aggregate. Ash can replace 20-40% of the asphalt binder by volume. Recent research suggests that a wide range of ash types can be used in asphalt. Fly ash can be added using conventional asphalt mixing equipment, although some modifications may be necessary. The market for asphalt is large; asphaltic concrete roads account for 94% of more than 2 million miles of paved roadways in the United States, and more than 500 million tons of asphalt are produced annually (NAPA 2015). This suggests a large potential market for fly ash that does not meet concrete-grade specifications, but the current use in asphalt is relatively small.

Research Organizations

University of Wisconsin-Milwaukee (UWM)
Milwaukee, WI
<http://cbu.ceas.uwm.edu/wordpress/>

UWM is engaged in a multiyear research project with EPRI to demonstrate the use of fly ash in asphalt. The research is evaluating the benefits of using several different fly ashes in asphalt mixtures using commonly accepted performance criteria, optimizing asphalt mixtures to enhance the durability of HMA pavements, developing an approach for efficiently introducing fly ash in HMA mixing plants at a mass production level, and evaluating the long-term effects of fly ash on performance and maintenance practices. UWM is also working with Wisconsin utilities, local paving companies, and the Wisconsin Department of Transportation to install test sections of road to demonstrate both installation and long-term performance. They have installed and evaluated performance of short road sections at We Energies power plant facilities.

Market Readiness

The technology to use ash in asphalt is commercially available. This technology has been available for decades, but it has achieved very low market penetration to date. Barriers may include the possible need for modifications of standard equipment, the lack of clear demonstrations of advantages and cost savings, and industry resistance to move away from conventional raw materials.

Nanotechnology

Description

Nanotechnology is one of the fastest growing areas in all aspects of research and product development. As previously discussed, very fine, high surface area fly ash particles are more reactive and are therefore higher-value products for additions to concrete. The full realm of potential nanotechnology applications is beyond the scope of this report, but one specific technology that was proposed in response to the Open Innovation RFP is described below.

Research Organizations

Polytechnique Montreal
Canada
www.polymtl.ca

Professor Jason Tavares at Polytechnique Montreal proposes to extract nanoparticles from fly ash and functionalize them in a photo-initiated reactor to improve their dispersion properties, thereby creating nanofluids for use in heat transfer applications. This research team has already performed a proof of concept in various types of ashes from a municipal solid waste incinerator. The approach is versatile and can accommodate a wide range of ash compositions.

The high cost of nanoparticles limits their use on a large scale. Nanoparticles from fly ash may not be ideal for certain specific applications where strict control on composition, particle size distribution, and morphology is required. But applications such as nanofluids for uses in heat transfer where the requirements are not as rigorous may be a good market for nanoparticles from fly ash.

The addition of solid particles to a liquid increases the overall thermal conductivity and also positively affects the critical heat flux and pool boiling properties (the nanoparticles serve as vapor bubble nucleation sites). This incremental improvement in heat transfer properties is significant in many fields where energy efficiency is crucial but the high cost of pure nanoparticles cannot be justified.

Market Readiness

This technology is conceptual—early proof of concept was performed with a similar material. Nanoparticles are a rapidly growing field and if successful these could become high-value applications. This application will only result in the reutilization of low volumes of fly ash, and it is likely many years away from commercialization.

7

SUMMARY AND DISCUSSION

This report has identified and described alternative and innovative technologies for the use of coal ash. These technologies are products and processes that currently are not significantly used in North Carolina, and in general have limited or no commercial markets in the United States. Eighteen technologies and more than 50 vendor products were described. Below is a summary of technologies and their prioritization based on market readiness, qualitative potential market size, and product value.

The technologies identified in this report represent a good cross section of alternative and innovative coal ash applications, but the list is not intended to be comprehensive. Discussion of specific vendor or product should not be construed as an endorsement of that product. New or modified ash use applications are appearing regularly as the industry adjusts to changing market conditions and R&D continues to improve on existing products and develop new ones. This framework was constructed to allow updating and revision on a regular basis, as promising new technologies and processes are identified or as market conditions change.

Moving New Technologies Forward

In most cases, successful applications will require active participation by the power company. Most alternative and innovative technologies entail greater time and financial investment by the power company, compared to simply selling the ash into a well-established commercial market such as conventional concrete. With the exception of some of the additional concrete products discussed in Group 1 below, most of the technologies will likely require the power company to become an active partner in development of the product and/or establishment of a commercial base. Depending on the technical maturity of the product, further development may necessitate a substantial investment in R&D. Establishment of a commercial base often may mean supporting co-location of a facility on or near a power plant, guaranteeing an adequate supply of ash for an extended period of time, and working with end users.

Because sustainable markets for these technologies are not fully developed, there is an inherent degree of business risk involved in these technologies. Development of commercial markets for alternative and new ash-based products typically takes a long time, particularly if the technology is competing with an existing, well-established commercial technology. There are several examples over the last two decades of sound technologies with significant capital backing that have failed to achieve sustained commercial success in the United States, most recently the CalStar bricks discussed in Section 2. Most of the technologies will require a commitment to working with the vendors to develop the products, obtain regulatory approvals, and communicate with end users to stimulate the nascent markets.

Technology Groupings

The summary below places the technologies presented in previous sections into four groups. Overall, the groups progress from lowest investment and business risk to highest investment and business risk, based on the authors' assessment. The primary consideration distinguishing the first three groups was technical maturity and market development, which together represent a measure of how much investment will be required and how quickly the products can be commercialized. Within each group, the technologies are further ordered by potential market size and value. The fourth group represents technologies that are either very early-stage products requiring significant basic R&D and long development time, or products that are well developed technically but have failed to gain traction in the U.S. market.

- Group 1: Market-Ready Technologies – Low Risk and Small Investment
- Group 2: Mature Technologies – Moderate Risk and Moderate Investment
- Group 3: Emerging Technologies – High Risk and Large Investment
- Group 4: Technologies with Limited Near-Term Market Potential

Group 1: Market-Ready Technologies

This group includes technologies that have penetrated existing markets in the United States to some degree, and require no basic research. Some product testing will be required to demonstrate and customize the applications for specific ash and market areas. In general, these applications are market-limited rather than technology-limited. These are primarily examples of specialty concrete products and fillers, of which there are many variations beyond those listed here. This is the lowest-risk group and may require little or no R&D investment by the power company. They may be pursued with established marketers to explore potential in a specific region. The markets for these products range from moderate to very small.

Flowable Fill and Foamed Concrete

Controlled low-strength materials (or flowable fills) and foamed concrete are specialty concrete products that can use higher amounts of fly ash that do not meet ASTM C618 specifications. They are typically used in place of conventional backfill materials in geotechnical and mining applications. Both processes are mature technologies in the United States. Their use is well established, and they are commercially available.

ACAA statistics indicate that about 84,000 tons of fly ash were used in flowable fill in the United States in 2014. It is not known how much fly ash is used for flowable in North Carolina and surrounding states. Foamed concrete applications identified in this assessment do not currently contain fly ash.

The size of the market for flowable fills and foamed concrete is believed to be small to moderate.

Assessment: Although not large, the market for fly ash in flowable fill is well developed, with existing vendor experience and flexible ash specifications. Increasing use of fly ash may be achieved by working with existing concrete vendors to identify market potential and establish applications. This alternative use requires little investment and is low risk. Addressing the quality control requirements for end users may help increase the sales of fly ash in this market.

Cenospheres and Ultra-Fine Fly Ash

Cenospheres and ultra-fine fly ash are used as fillers in a wide range of products. Common mineral fillers include ground and precipitated calcium carbonate, talc, mica, kaolinite, natural and synthetic glass, feldspar, and titanium dioxide. Fly ash competes in the same market as calcium carbonate. These materials are used as fillers in plastics, controlling shrinkage and contributing to strength while reducing costs. Foams, rubber products, coatings, paints, roofing shingles, siding, carpet backing, and synthetic wood also use fillers.

Cenospheres are a lightweight filler material that commands a very high price. However, they only make up about 2% of fly ash. They are collected from ash ponds by drawing them into thick mats and skimming them off the pond surface. As ponds are replaced by landfills, cenospheres will become harder and more costly to collect. Dry separation of cenospheres is in the early research stage.

Ultra-small filler applications require significant processing of the fly ash to reduce particle size and remove undesirable impurities. Typical particle size is on the order of a median diameter of 5 microns. They are most applicable in applications where color is not critical. Ultra-fine fly ash fillers command a high price.

Assessment: The market for selling cenospheres and ultra-fine fly ash is relatively small but high value. Beneficiation (size reduction, reducing carbon content) and strict quality control to ensure uniformity are required. These products represent low risk and can be pursued through discussions with established vendors, however, they will only consume a small volume of fly ash.

Superpozzolans

Superpozzolans consist of fly ash that has been beneficiated to the point where its performance is at the level of meta-kaolin and silica fume. The level of beneficiation required typically consists of air classification of dry fly ash to obtain a fraction with mean particle size in the range of 3 to 5 μm .

This is a mature technology used primarily in the southwest United States. Superpozzolan sizing is performed by the concrete vendor, and as such represents a low risk and investment to the power company. However, there is currently only a small market for specialty applications in the United States. Production costs are higher than for conventional ASTM-compliant fly ash, although the product also commands a premium price. Note that the silica fume market is expected to grow, which can result in an increase in the demand for fly ash-based superpozzolans as an alternative.

Assessment: Like cenospheres and ultra-fine materials, this is a high-value product with a small market. This product has low risk, and can be pursued through discussions with an established concrete vendor.

Group 2: Mature Technologies

This group consists of products that are well developed technically and have demonstrated some market potential in the United States. They do not require basic research, but generally may require some R&D to further develop, test, and/or demonstrate the products. These products are typically entering existing markets for similar materials that do not use ash as a raw material. Accordingly,

the primary market development activities are aimed at demonstrating equivalent performance at a lower cost, or better performance at a similar or slightly higher cost. Vendors may be well-established companies, or they may be smaller start-ups seeking partnering opportunities. Development of these technologies and products represents a moderate risk and investment.

Manufactured Aggregates

Manufactured aggregates are not a new concept. There have been many processes for producing manufactured fly ash aggregates developed in the past. They generally produce a lightweight aggregate for use in a variety of construction materials and activities, and can contain up to 95% fly ash. The process involves agglomeration of fly ash particles by addition of a binder and other additives, and in some cases includes a sintering step. Ash specifications are less strict than for conventional concrete, and bottom ash can also be used.

Manufactured concrete aggregates using fly ash are a mature technology that has been marketed commercially in various forms. A recent study by the Freedonia Group (2016) indicates that the market for aggregates worldwide is expected to grow at an annual rate of 5.2%, and that the market for alternative aggregates, including those containing fly ash, will grow at twice the rate as the market for sand and gravel. Fly ash aggregates have achieved some degree of commercial success in the past, but have generally not been a sustainable business, likely due to the low cost of natural aggregates.

Assessment: Despite the simplicity of the technology and the large potential market, unless the manufacturing is subsidized this option is probably not cost-competitive in the Southeast where low-price natural aggregates are available.

Geopolymers

Geopolymers are a cementitious binder that is an alternative to portland cement. Concrete made with geopolymer cement is marketed as a high-strength material with good durability and lower carbon footprint than portland cement-based products. Geopolymers are well suited for specialty and precast applications, such as flame-retardant insulation panels, corrosion-resistant concrete, high-temperature refractory, sprayable coatings for concrete pipe protection, and precast concrete pipe, blocks, and bricks. Geopolymers use primarily Class F fly ash, although Class C can also be used in some applications.

Commercialization has been slow despite the large amount of ongoing research and literature related to geopolymers. In the United States this may be largely related to the well-established ready mixed concrete infrastructure based on portland cement, while the geopolymer process requires different ingredients and placement methods. Most importantly, the geopolymer process requires the use of highly caustic liquids that can be difficult to handle, although recent research and product development is experimenting with powdered alkaline sources.

Assessment: The current market in the United States and worldwide is limited but growing. Geopolymer products have many desirable performance characteristics, especially in high-temperature and highly corrosive environments. The technology has been, and continues to be, extensively researched in the United States and worldwide. It is expected that the geopolymer industry will continue to grow as the products become more flexible and adapted to the U.S. construction market. These products have the potential to use large volumes of fly ash.

Masonry Units

Concrete bricks, pavers, and other masonry units are traditionally made from the same ingredients as conventional concrete: portland cement, water, sand, and aggregate. Fly ash can be substituted for the portland cement, sand, and aggregate, with very high replacement percentages, in some cases in excess of 80% or 90%. Class C fly ash is generally used in press-molded bricks and pavers. Class F fly ash can be used for press-molded pavers with the use of a secondary binder. Class F fly ash can also be used in kiln-fired clay-based bricks.

Low carbon levels are preferred for ambient temperature concrete masonry products to avoid undesired dark colors in the final product. Conversely, higher LOI levels can possibly augment firing in kiln-fired products.

Fly ash masonry has been researched and marketed sporadically in the United States over the last two decades, but has not achieved widespread acceptance in the marketplace. Brick production facilities are usually co-located with the fly ash source. The use of fly ash in bricks is growing rapidly in India, due to a mandate by the Indian government.

Assessment: Bricks and pavers represent a mature technology that is marketed as an environmentally friendly alternative to conventional masonry products. Several technologies to produce bricks and pavers using various ash types and processes have been developed. However, there remain market barriers to significant commercial growth in the United States. Continued evaluation of brick and paver products is warranted given the potential for using large quantities of fly ash; however, the past failures to gain a sustainable foothold in the market suggest a degree of risk.

Alternative Cements

Alternative cements represent a wide range of cementitious binders that are not based on portland cement. In some cases, they use only fly ash and proprietary additives in the binder; in others, they use fly ash at high replacement for portland cement along with other ingredients such as limestone or ground glass. These cements are often marketed as environmentally superior due to energy savings and a smaller carbon footprint than portland cement.

Alternative fly ash-based cements can be used in a variety of concrete products. They have a small share of the cementitious market, and like geopolymers are often used for precast and specialty products in the United States.

Assessment: Alternative cements command a small market relative to portland cement. Like geopolymers, widespread use of alternative cements in the United States is limited due to difficulties in integrating new materials and nonstandard processes into the ready mixed concrete supply chain. Alternative cements appear to have less potential for use of bituminous coal fly ash than geopolymers.

Asphalt

Fly ash can be used as mineral filler in the production of hot-mix asphaltic concrete. The fly ash replaces some of the asphalt binder and polymers, resulting in about 1 to 3 percent of the asphaltic concrete mix. The introduction of fly ash reduces overall cost and improves performance of the asphaltic concrete. Research suggests that use in asphalt is not sensitive to ash type or variability.

This is a mature technology that can use conventional asphalt equipment. The potential market is relatively large, on the order of 1 million tons of fly ash annually or more. However, current use is very small.

Assessment: Although this is a well-established technology with a potentially large market, there has been very little market penetration to date. Increasing use will require actively working with suppliers and end users on a regional basis, and will likely require local demonstrations of asphalt mixing and performance of paved surfaces. If successful, this can use a moderate amount of ash that does not meet concrete specifications.

Group 3: Emerging Technologies

This group includes products and technologies that have potential for large or high-value markets, but will likely require a significant investment in basic research and market development. These are farther from commercialization than Group 2 technologies, will require more investment to bring to market, and will have a commensurate level of business risk.

Wastewater Brine Stabilization/Solidification

New effluent guideline regulations require power companies to treat wastewaters from flue gas desulfurization systems. One option is volume reduction followed by solidification/stabilization (S/S) of the concentrated brine. Fly ash and other CCPs may represent the best alternative for S/S of the brines and high-solubility solids.

This technology can potentially use large volumes of CCPs, with the dual benefit of managing both the CCP and the wastewater. The success of this technology depends on encapsulation of the brine and long-term stability in the landfill environment. S/S is already used in the industry to stabilize scrubber sludge and more dilute wastewaters, but it has not been demonstrated for wastewater brines.

EPRI and others are researching optimization of CCP use in the S/S process. Although this research is in the early stages, the work is being fast-tracked due to pressing needs imposed by recent effluent guidelines regulations.

Assessment: Although this technology has not yet been demonstrated, there is a concerted effort by the industry and vendors to develop viable solutions quickly. If successful, this application will utilize significant quantities of CCPs, while reducing salt and trace element release from both media.

Metal Matrix Composites

Fly ash is used as a filler in metal matrix composites to increase the hardness and the abrasion resistance of the lighter-weight materials. In addition, fly ash composites are significantly lower in cost than the alternative, aluminum-silicon carbon composites. This application utilizes a fraction of fly ash between 10 and 100 micrometers (preferably between 20 and 40 micrometers), with no LOI, low CaO content, and almost no cenospheres. Hence, a certain degree of preprocessing of the ash is required.

Metal matrix composites with fly ash are marketed for wear-resistant automotive parts, such as drums, breaks, engine blocks, discs, and pistons. This application has been researched for more than two decades, but there appears to be little commercialization in the United States. The use in automotive parts has been commercialized to a degree in Australia.

Assessment: Although this technology has been available since the 1990s, commercialization is limited. Further R&D to facilitate product development and acceptance is required. This is a high-value use, but the volumes likely are not large, and significant preprocessing is required.

Proppants

Proppants are a relatively new product, consisting primarily of quartz sand particles used to stabilize wells and hold fractures open in the production of shale gas and oil by fracking technology. These materials represent a moderate-size industry; an estimated 45 million tons of proppants were used in 2013.

The use of fly ash in proppants is being extensively researched, as evidenced by the large amount of patents issued on this topic. Most of these patents refer to the use of fly ash as a potential ingredient in the fabrication of synthetic proppants. Proppants require uniform size and good quality control during production, requiring some level of fly ash preprocessing.

The recent steep decline in oil and gas prices has resulted in a slowdown in shale gas and oil production, significantly impacting the proppant market. When prices recover, it is expected that proppant use will increase because there is a trend toward increasing proppant tonnages per well. There is also a trend toward finer particle size materials, which could favor fly ash proppants. Fly ash proppants currently are not being used in the industry.

Assessment: Due to the increasing reliance on fracking in the United States, this use has a moderate market size potential for fly ash. Additional investment in R&D is needed to establish technical specifications for fly ash in the proppant marketplace.

Polymer Composites

Fly ash polymers can be used as flame retardants in organic foams used as insulators, replacing traditional retardants based on halogenated organic compounds. They can also be used in more familiar building applications, such as roofing, siding, decking, chair rail moldings, and decorative pieces. These uses are still in early-stage R&D and have not been commercialized, but offer a wide range in potential moderate to high-value applications.

Assessment: These products are at the early research stage and not yet commercial, and they will require significant investment. Given the potential market size and value, research efforts should be monitored for significant developments.

Group 4: Technologies with Limited Current Market Potential

Technologies in this group may be technology-limited or market-limited. In either case, these are considered the most difficult to commercialize in the short term. Market-limited technologies may be well developed but have shown to date an inability to gain acceptance in the United States. That does not preclude their future acceptance, but suggests there may be underlying market constraints. The technology-limited products are at early-stage development and will require substantial R&D investment. They are considered to be at least five to ten years or more from commercial implementation and may never be economically feasible.

Autoclave Aerated Concrete (AAC)

Autoclaved aerated concrete is a mature technology used to make blocks and panels with a formulation that can result in as much as 70% of fly ash by weight in the final product. These blocks and panels are very popular in construction in Europe and Asia due to their light weight, low cost, and low thermal conductivity.

The construction industry in the United States is very different than in Europe, and the AAC technology has not met with similar commercial success here. In 2006 there were five manufacturers of AAC blocks in the United States. That has now decreased to only one manufacturer, and they do not use fly ash in their formulation

Assessment: Although the technology is mature and well accepted outside the United States, there is little or no market in the United States. The potential market for AAC products could be moderate to large if they attain industry and public acceptance, but there are no current indications that such a scenario will occur soon. Market conditions should be monitored to identify new products and vendors for opportunities.

Zeolites and Water Treatment

Fly ash can be used as a precursor for manufacturing synthetic zeolites if it can be processed to increase its ion exchange capacity. Fly ash-based zeolites generally compete with low-priced natural zeolites for adsorption applications in agriculture and water treatment, and with high-priced synthetic zeolites for specialty applications.

The chemistry for manufacturing zeolites from fly ash is well understood. Research in the past has proven the feasibility of producing fly ash-based zeolites, but research on process technology has been lacking. Therefore, the processes have not been sufficiently optimized to result in competitive production schemes. Fly ash zeolites are still too expensive to compete with abundant natural zeolites, and have not been fully developed to compete with specialty synthetic zeolites that offer high purity for higher prices.

Assessment: Although the technology to process fly ash into zeolites has been developed, the production process has not been optimized, resulting in higher cost and lower quality than for other synthetic zeolites. Additionally, the market for fly ash-based zeolites is not well defined, and the advantages of using fly ash are not clear. As a result, there is limited market potential at this time. However, given the variety of potential applications, ongoing R&D and product development should be monitored to identify future opportunities, particularly in wastewater treatment.

Metals Recovery – Aluminum, Magnesium, and Other Metals

The value of metal content within fly ash depends upon the concentrations of elements, which can vary considerably depending on the source of coal burned. Alumina, iron, silica, titanium, gold, and magnesium can be recovered through well-known extraction processes.

A commercially scaled-up process for the recovery of germanium from coal ash is being undertaken in China and Russia. Aluminum is being recovered from high-alumina fly ashes in China, and a process is being developed in Canada for commercialization in the United States. Several companies claim to have technologies for metal extraction from fly ash; however, there are no companies in the United States that have scaled up for commercial production, suggesting that these processes may not be economically viable.

Assessment: This group of technologies has been the subject of speculation and R&D activities for more than 20 years. They are currently being pursued outside the United States, but no commercial production of these materials from fly ash is taking place in the United States. The technologies for extraction are understood, if commodity prices increase to make recovery economically attractive. One significant barrier in the United States is management of the large amount of waste produced by most of these operations.

Rare Earth Elements (REE) Recovery

Due to the high demand for many rare earth elements, coal combustion fly ash represents a potential and readily available source of this material. Small amounts of rare earth elements are used in a variety of common devices such as computer memory, DVDs, mobile phones, hybrid cars, wind turbines, and rechargeable batteries. They are also used in many military applications.

Many companies and universities have been engaged in R&D due to the REE supply shortage and price increase in about 2010. The price and supply concerns have since subsided, and the one hard rock mine producing REEs in the United States ceased operations in 2015. The 2010 supply scare does, however, suggest that identifying a domestic supply of REEs could potentially become important again in the future. The Department of Energy has a large research program in this area and recently funded ten proposals to recover REEs from fly ash and coal-related wastes.

Assessment: Recovery of REEs from fly ash is at the early research stage and will require significant investment in R&D and change in market conditions before it is commercial. REEs are present in fly ash in trace quantities, and management of wastes generated during their recovery is a significant concern. It is unlikely that a commercially viable process will emerge in the near term under the current supply and demand conditions. However, as evidenced by the market volatility over the last decade, market conditions can change rapidly for this commodity. The DOE research is designed to identify feasible technologies in the long-term.

Nanotechnology

Nanotechnologies are a significant area of research. One proposed application encompasses using a fraction of fly ash to enhance heat transfer in nanofluids. This technology is at the very early R&D stage, and even when fully developed will only use a very small fraction of ash.

Assessment: Given the large research interest in nanoparticles, this technology warrants tracking, but it is not a significant commercial possibility in the near term.

Plasma Arc/Vitrification

Vitrification systems are commercially available and are currently being used to treat municipal solid waste ash in Japan on a continuous commercial basis. However, none of these systems are currently working for the application of vitrifying coal ash. The basic technology is well developed but is still at early commercial development stage level for fly ash. There are some vendors that are offering commercial systems for coal ash, although none have demonstrated commercial operations.

Ash vitrification is a costly technology that is hard to economically justify based on ash use alone. It is usually performed as part of a remediation program to reduce or eliminate trace element leaching from the ash, with use of the final product as a secondary consideration. The vitrified ash can be used to produce glassy aggregates for the construction industry, but that is not a robust economic alternative for ash use. Some vendors have proposed producing rock wool type insulation material (by spinning the vitrified ash), which represents a higher-value product. Plasma arc technologies are also proposed as part of an REE recovery technology that is being researched under the major research initiative sponsored by the U.S. DOE describe above.

Assessment: Use of plasma arc and vitrification technologies are unlikely to be an economical alternative for creating fly ash products, unless multiple high-value products with large markets are produced.

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REFERENCES

- American Coal Ash Association (ACAA), 2015. 2014 Coal Combustion Product (CCP) Production and Use Survey Results. Accessed on December 22, 2015 at <http://www.aaa-usa.org/>
- American Concrete Institute, 2013. ACI 229R-13. *Report on Controlled Low-Strength Materials*.
- Bai, G., Y. Qiao, B. Shen, and S. Chen, 2011. *Thermal decomposition of coal fly ash by concentrated sulfuric acid and alumina extraction process based on it*, Fuel Processing Technology, V. 92, No. 6, pp. 1213-1219.
- Canadian Intellectual Property Office (CIPO), 2015. *Processes for Preparing Alumina and Magnesium Chloride by HCl Leaching of Various Materials*, Patent 2885255 Summary. <http://www.ic.gc.ca/opic-cipo/cpd/eng/patent/2885255/summary.html>.
- Circeo, L., 2010. Plasma Arc Gasification, Presentation accessed at <http://documents.mx/documents/plasma-arc-gasification-louis-j-circeo-phd-principal-research-scientist-electro-optical-systems-laboratory-january-2010-director-plasma-applications.html>.
- Davidovits, J., 1991. *Geopolymers: Inorganic polymeric new materials*, Journal of Thermal Analysis V.37, pp. 1633-1656.
- Ecologic Tech 2016. <http://ecologic-tech.com/faqs.html>. Accessed May 20, 2016.
- EPRI, 1990. *Market Opportunities for Fly Ash Fillers in North America*, EPRI, Palo Alto, CA: 1990. GS-7059.
- EPRI, 1994. *Solid Processing of Metal Matrix-Fly Ash Particle Composites*, EPRI, Palo Alto, CA: 1994. TR-104409.
- EPRI, 1999. *Development of New Industrial Ashalloy Material Using Fly Ash Cenospheres "Lead Lite" Project*, EPRI, Palo Alto, CA: 1999. TE-114154.
- EPRI, 2000. *Evaluation of Existing Structural Design Methods for AAC panels: Designing with Autoclaved Aerated Concrete*. EPRI, Palo Alto, CA: 2000. 1000306.
- EPRI, 2002. *Ash-Derived Zeolites for Odor Control and Fertilizer Delivery*. EPRI, Palo Alto, CA: 2002.1004401.
- EPRI, 2015. *Utilization of Geopolymer Concrete in Solidification/Stabilization of Sorbent Impacted Fly Ash and Power Plant Wastewater Treatment Solids*. EPRI, Palo Alto, CA: 2015. Prepared for Duke Energy.
- EPRI, 2016a. *Duke Energy Coal Combustion Product Management Study: Phase 1 - Market Assessment*. EPRI, Palo Alto, CA: 2016. Prepared for Duke Energy.

References

- EPRI, 2016b. *Duke Energy Coal Combustion Product Management Study: Phase 2 - Beneficiation Technologies*. EPRI, Palo Alto, CA: 2016. Prepared for Duke Energy.
- Freedonia Group, 2016. *World Construction Aggregates*, Press release dated April 20 2016, <http://www.freedoniagroup.com/DocumentDetails.aspx?ReferrerId=FE-STAN&studyid=3389>.
- Hanus, G. and T. Mustoe, 2003. *Solutions Co's Commercial Ash-Melting Experience in Japan*, 16th International Symposium on Plasma Chemistry Taormina, Italy June 22-27 2003.
- Hrairi, M., M. Ahmed, and Y. Nimir, 2009. *Compaction of fly ash–aluminum alloy composites and evaluation of their mechanical and acoustic properties*, *Advanced Powder Technology*, V. 20, No. 6, pp. 548-553.
- Kruger, R., M. Hovy, and D. Wardle, 1999. *The Use of Fly Ash Fillers in Rubber*, 1999 International Ash Utilization Symposium, www.flyash.info.
- Kulkarni, S., J. Meghnani, and A. Lal, 2014. *Effect of Fly Ash Hybrid Reinforcement on Mechanical Property and Density of Aluminium 356 Alloy*, *Int. Conf. on Advances in Manufacturing Materials Engineering*, V. 5, pp. 746-754.
- Liu, H., W. Burkett, and K. Haynes, 2005. *Improving Freezing and Thawing Properties of Fly Ash Bricks*, *World of Coal Ash*, April 11-15, 2005, Lexington, KY.
- Lokeshappa, B. and A. Dikshit, 2012. *Single Step Extractions of Metals in Coal Fly Ash*, *Resources and Environment*, V. 2, No. 2, pp. 1-8.
- Matjie, R., J. Bunt, and J. van Heerden, 2005. *Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal*, *Minerals Engineering*, V. 18, No. 3, pp. 299-310.
- McLellan, B., R. Williams, J. Lay, A. van Riessen, and G. Corder, 2011. *Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement*, *Journal of Cleaner Production*, V.19, pp. 1080-1090.
- Mehta, P. and P. Monteiro, 2005. *Concrete: Microstructure, Properties, and Materials*, McGraw Hill Professional, 659 p.
- Moutsatou, A., G. Itskos, N. Koukouzas, and P Vounatsos, 2009. *Synthesis of aluminum-based metal matrix composites (MMCs) with lignite fly ash as reinforcement material*, *World of Coal Ash*, May 4-7, 2009, Lexington, KY.
- National Asphalt Pavement Association, 2015. http://www.asphalt pavement.org/index.php?option=com_content&view=article&id=14&Itemid=33. visited 3/24/2015
- National Rural Electric Cooperatives Association (NRECA), 2013. *Coal Combustion Ash Processing Technologies: A Review of the Current Status and Future Potential*, Project 12-04, December 2013.
- Oberlink, A., T. Robl, R. Jewell, B. Marrs, and J. Wiseman, 2015. *Fly Ash Derived Ceramic - Polyurethane Foam Composite Insulation*, *World of Coal Ash*, May 5-7, 2015, Nashville, TN.

- Pandey, B., S. Kinrade, and L. Catalan, 2012. *Effects of carbonation on the leachability and compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes*. *Journal of Environmental Management*, 101, 59–67.
- Ramenzanianpour, A., 2013. *Cement Replacement Materials: Properties, Durability, Sustainability*, Springer Science & Business Media, 336 p.
- Ramme, B., and M. Tharaniyil, 1999. *Wisconsin Electric Power Company Coal Combustion Products Utilization Handbook*, Wisconsin Electric Power Company, 216p.
- Rapoport, J., 2013. *Fly Ash Use in Commercial Masonry and Hardscape*, EPRI Fall Advisory Meeting, October 8, 2013, Pittsburgh, PA.
- Slag Cement Association, 2016. *Slag Cement and Fly Ash*. <http://www.slagcement.org/>
- Sobolev, K., F. Ismael, J. Bohler, A. Faheem, and A. Covi, 2013. *Application of Fly Ash in ASHphalt Concrete from Challenges to Opportunities*, World of Coal Ash Association, Lexington, KY, May 2013.
- Tapkin, S., 2008. *Improved Asphalt Aggregate Mix Properties by Portland Cement Modification*, *Canadian Journal of Civil Engineering*, pp. 27-40.
- Tolhurst, L., 2015. *Commercial Recovery of Metals from Coal Ash*, World of Coal Ash, May 5-7, 2015, Nashville, TN.
- United Kingdom Quality Ash Association, 2005. Technical data sheet 7.1.
- United Kingdom Quality Ash Association, 2014. Annual Ash Statistics.
- United States Department of Energy, 2015. DOE Selects Projects To Enhance Its Research into Recovery of Rare Earth Elements from Coal and Coal Byproducts, Press Release dated December 2, 2015, accessed at <http://www.netl.doe.gov/newsroom/news-releases/news-details?id=55360995-ae95-4722-8370-58d0b58fb82f>.
- United States Geological Survey, 2016. Minerals Commodity Summary, accessed at http://minerals.usgs.gov/minerals/pubs/commodity/rare_earth/mcs-2016-raree.pdf.
- Yao, Z., M. Xia, P. Sarker, and T. Chen, 2014. *A review of the alumina recovery from coal fly ash, with a focus in China*, *Fuel*, V. 120, pp. 74-85.
- Zhao, Y., J. Jow, X. Cai, and S. Lai, 2015. *Fly Ash-based Geopolymer Foam Technology for Thermal Insulation and Fire Protection Applications*, World of Coal Ash, May 5-7, 2015, Nashville, TN.

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