

# Transforming CCBs in Maryland to Enhance Beneficial Use

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## ABSTRACT

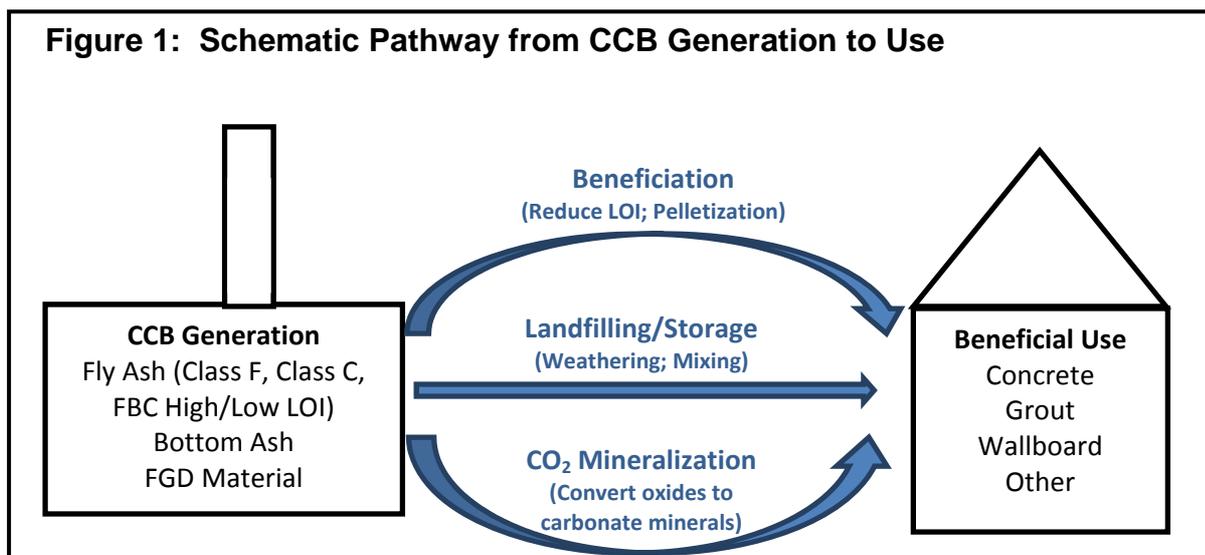
Beneficial use, like other recycling processes, involves intermediary steps that may alter the physical and chemical nature of the material to be reused. Some processes are necessary steps required to prepare the material for its eventual applications. Other transformations are a consequence of the storage, transportation, or intermediary uses of the material that may hinder or enhance its utility for an ultimate beneficial use.

This paper will examine two processes that have been influential in the transformation of Maryland coal combustion by-products (CCBs) resulting in increased beneficial use. Maryland boasts two successful ash beneficiation facilities, each using different approaches to reduce the loss-on-ignition (LOI) content of Class F fly ash resulting in a highly desirable raw material for the State's successful concrete industry. Maryland has also benefited from a successful program to mine landfilled CCBs from one power plant; a partnership that has benefitted both the power generator and the industry user of CCBs. Landfilled or stored ash can undergo physical and chemical changes that have implications for future users.

Additionally, attention will be given to the transformation of CCBs through mineralization of CO<sub>2</sub>. While this process is currently in pilot scale studies, recently published data suggest that it is technically and economically feasible to use alkaline CCBs to capture and store CO<sub>2</sub> from power plant emissions in the form of stable carbonate minerals. The potential benefits and barriers to utilizing such a process at Maryland power plants will be discussed, along with considerations for the ultimate fate of mineralized CCBs.

## INTRODUCTION

Recycling is rarely a single-step process. Common recyclables like glass, plastic, and metal must be sorted, broken or shredded, and melted before reuse. Paper is shredded and wetted into a pulpy mass that is then washed, pressed, and dried. Likewise coal combustion by-products (CCBs) may require intermediary steps between their generation at coal fired power stations and their eventual beneficial uses. Some beneficial uses allow for CCBs to be taken directly from the power plant with, perhaps, only a small amount of conditioning (i.e. addition of water) to control fugitive dust in transport. However, in some cases, the type of beneficial use, or the nature of the CCBs themselves requires active treatment processes like beneficiation to make them suitable for the use (Figure 1). Ash beneficiation refers to any process that alters the physical or chemical nature of CCBs, making them better suited for a particular use. An oft-cited example (and one that has been key to beneficial use in Maryland) is reduction of unburned carbon (LOI) in fly ash, making it a more attractive raw material for ready-mix concrete producers. Other beneficiation processes exist, such as the pelletization of flue gas desulfurization material (FGD) to make a fertilizer product that is more readily sold to and used in agricultural applications.<sup>1</sup>



Other transformations are more passive. CCBs that are not destined for a specific beneficial use immediately after generation are generally disposed in landfills or ponds. In time, new beneficial use applications may be developed or demand for CCBs by industry may increase to a point where these CCBs formerly disposed as waste, can be considered a valuable commodity to mine. Because CCBs are fine-grained solids generated at high temperatures, time elapsed since generation, exposure to atmospheric conditions, and exposure to water (particularly in the case of ponded ash) can cause physical and chemical changes to the CCBs that must be taken into account.

Maryland enjoys a high rate of CCB beneficial use (87% in 2013). This is largely due to the presence of industries like cement and wallboard manufacture in the region that are

eager to use fly ash and flue gas desulfurization materials to make their products. Maryland has also been successful using both beneficiation and recovery of previously disposed ash to increase its beneficial use rates, and its rate of encapsulated (i.e. concrete and grout) rather than unencapsulated uses. As Maryland looks to the future, other transformations like carbon dioxide (CO<sub>2</sub>) mineralization are under study to increase Maryland's use of its alkaline CCBs.

## OVERVIEW OF CCB PRODUCTION AND USE IN MARYLAND

Maryland's 7 coal-fired power plants generate about 1.5 million tons (1.4 million metric tons) of CCBs annually. The variety and quantity of CCBs produced in Maryland in 2013 is shown in Table 1.

**Table 1: Types and amount of CCBs produced in Maryland (2013)**

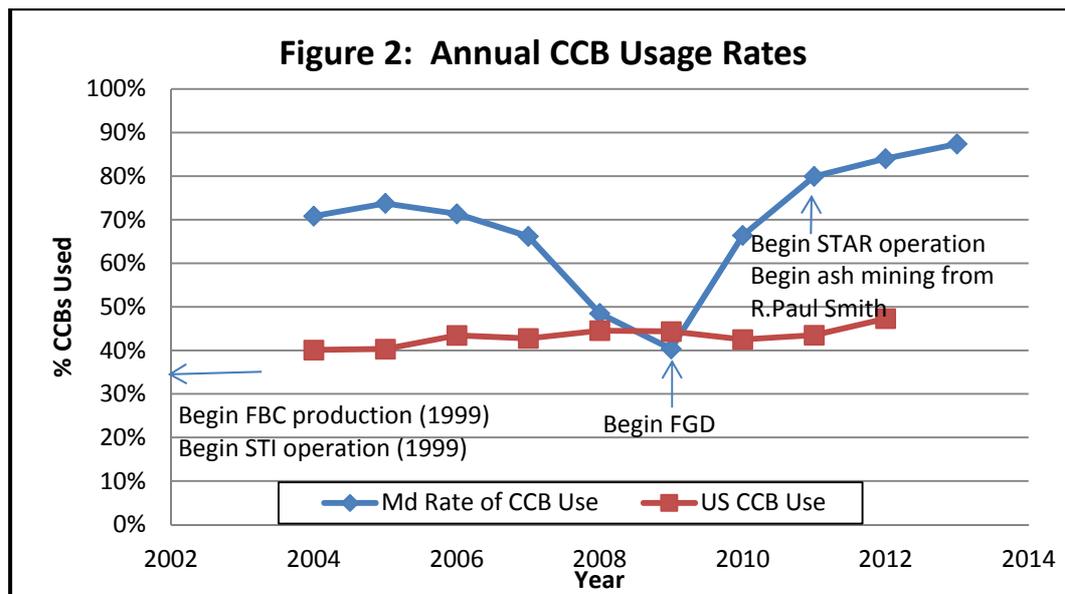
CCB Type	Quantity (tons)	Quantity (metric tons)
<i>Non-Alkaline CCBs</i>		
Class F Fly Ash	484,110	439,175
Class F Bottom Ash	175,158	158,900
Boiler Slag	8,043	7,296
FGD Material	414,249	375,798
<i>Alkaline CCBs</i>		
Class C Fly Ash	9,235	8,378
FBC fly ash	291,630	264,561
FBC bottom slag ash	122,985	111,570

Maryland power plants have made a number of upgrades to meet state and federal clean air standards. These changes have had impacts on the properties of the CCBs produced. The use of low-NOX burners in Maryland, beginning in the mid-1990's, caused an increase in the LOI content of Class F fly ash from certain plants. Installation of flue gas desulfurization (FGD) scrubbers in 2009 introduced an entirely new stream of CCBs – FGD solids (i.e. synthetic gypsum). Replacement of bituminous coal from Appalachia to sub-bituminous coal from the Powder River Basin at another plant resulted in the first production of Class C ash in the state in 2009.

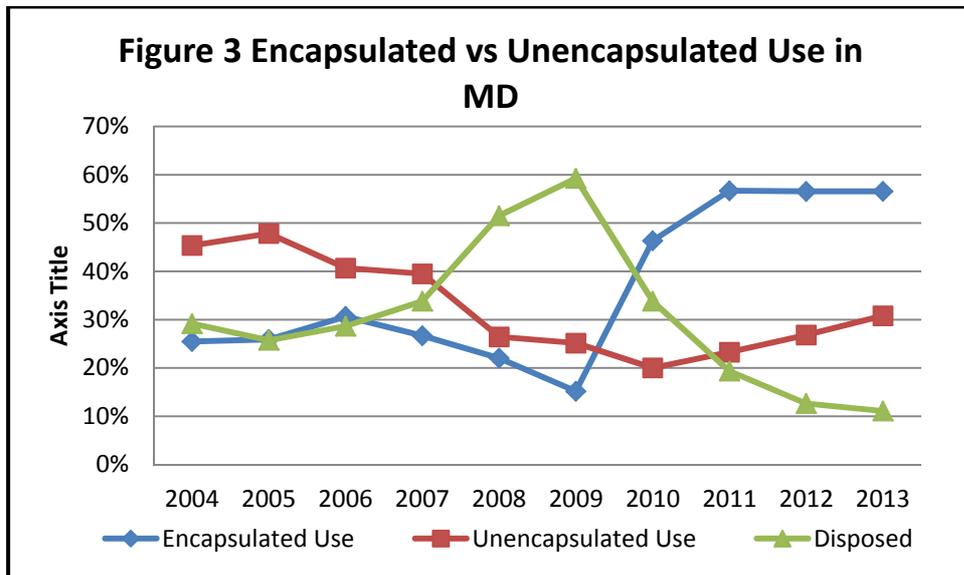
While the introduction of FGD scrubbers increased the overall volume of CCBs produced in Maryland, this material was quickly absorbed by regional wallboard manufacturers as a raw material. Some FGD material was also used in agricultural applications. The high-LOI Class F ash and the Class C fly ash have proven somewhat more challenging to use.

In spite of the challenges presented by changes in CCB production over the past 10 years, Maryland has consistently achieved a high rate of beneficial use of its CCBs. As shown in Figure 2, Maryland's beneficial use rates have ranged from 40% to 87% and have generally exceeded 60%. By comparison, US rates are generally steady between 40% and 50%.<sup>2</sup> It is worth mentioning that the decline in CCB use in Maryland between

2007 and 2009 coincides with the completion of several large scale reclamation projects as well as the preparation to install FGD scrubbers at 4 plants (these installations were completed in 2010). The increase in beneficial use from 2010 forward is related to the installation and operation of the STAR ash beneficiation facility (discussed in greater detail below) as well as the sale of FGD material to the wallboard industry once all FGD scrubbers were fully operational.



Just as the types of CCBs produced in Maryland have changed over time, the predominant types of uses have changed as well. The predominant types of beneficial uses in the state have shifted from predominantly unencapsulated uses like structural fill and traction control for snowy/iced roads to predominantly encapsulated uses, like the production of concrete, wallboard, and grout (Figure 3). The decline in unencapsulated uses from 2007 to 2010 is primarily due to the ending of some large scale reclamation projects, as mentioned above. The increase in unencapsulated use from 2010 through 2015 is due to a slight increase in ash production at the Warrior Run power plant, which uses 100% of its alkaline fluidized bed combustion (FBC) ash for coal mine reclamation. Also, as mentioned above, the decline in encapsulated uses from 2007 to 2009 coincides with the period leading up to installation of FGD scrubbers as well as the STAR ash beneficiation facility.



Several factors have driven the change in beneficial use applications in Maryland: changes in the types of CCBs available, changes in industry demands, and changes in the regulatory status of the material and certain use applications. While they may not have been primary drivers for the change in beneficial uses, CCB transformations have certainly played a role in this change. The availability of beneficiated, low-LOI Class F fly ash has helped to increase the use of ash in concrete in the State; meanwhile the booming cement/concrete industry demand for fly ash has made recovery of ash from former fill areas economically advantageous.

### FLY ASH BENEFICIATION

The use of low-NOx burners, which reduce the emission of smog-producing constituents in flue gas, has greatly improved air emissions from coal fired power plants; however, they create new challenges for beneficial use of CCBs. Low-NOx burners operate at lower temperatures than standard burners, leaving more unburned carbon or LOI. The ASTM C618 standard for fly ash to be used in concrete is < 6%, although LOI < 3% is generally considered most desirable for marketing to the concrete industry.<sup>3</sup> LOI levels at Maryland power plants using low-NOx burners have been measured as high as 15%.<sup>4</sup>

A variety of ash beneficiation techniques and technologies have been developed to reduce the level of unburned carbon in fly ash. These processes benefit electricity generators by converting a waste product to a marketable commodity; they benefit the cement and concrete industries by preserving a supply stream of high-quality recycled ingredients for their products.

Maryland boasts two ash beneficiation facilities that use two distinct methods to reduce LOI. Each of these plants sells 100% of its processed ash to the concrete industry. Together they helped to ensure that nearly 80% of the Class F fly ash produced in Maryland in 2013 was beneficially used.

### **STI Ash Beneficiation Facility**

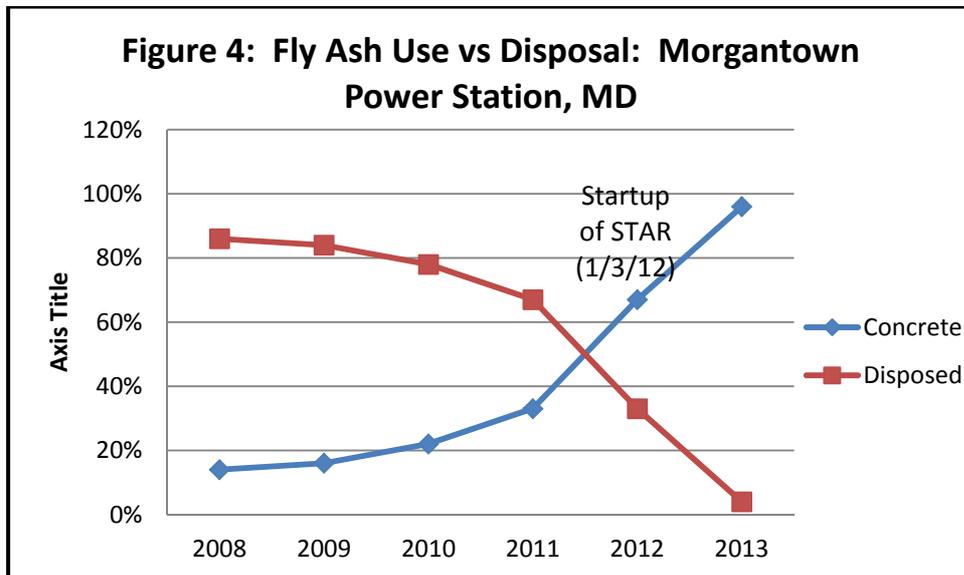
The Separation Technologies, Inc. (STI) facility, located near Glen Burnie, Maryland was constructed in 1999 and operates in association with two nearby coal fired power plants, both owned and operated by the Raven Group. The majority of fly ash processed at the facility is produced at the Brandon Shores power plant; some ash is also brought in from the H.A. Wagner power plant. The STI facility uses electrostatic separators to remove unburned carbon from the remaining mineral components of the ash. The process is able to reduce the LOI content of fly ash from as high as 25% to around 2%. Unburned carbon is returned to the power plant as fuel, while the low-LOI processed ash is sold to the concrete industry.<sup>5</sup>

In 2013 the STI facility processed and sold over 170,000 tons (over 154,000 metric tons) of fly ash. Over 12,000 tons (over 10,000 metric tons) of material high in unburned carbon was returned to the power plant as fuel. For the last three years, 80% to 90% of the fly ash produced at the Brandon Shores plant has been processed at the STI facility and sold for the production of ready-mix concrete.

### **STAR Ash Beneficiation Facility**

The STAR facility was constructed as an addition to the Morgantown Generating Station in southern Charles County, Maryland. It was constructed in 2012 and primarily processes ash from the Morgantown power plant, although some ash from the Chalk Point power plant (located in Eagle Harbor, Maryland) and Dickerson power plant (located in Dickerson, Maryland) are also processed, as capacity allows. All three power plants are owned by NRG Energy. The STAR facility uses an innovative re-burning process developed by the SEFA Group, Inc. (SEFA) to remove the unburned carbon. The STAR facility at the Morgantown power plant was only the second facility of this type to be constructed (the first being in Columbia, South Carolina). The Maryland facility is larger and processes about twice as much ash as the South Carolina facility.<sup>4</sup>

After the initial start-up period, the plant operations are self-sustaining (i.e. heat from the ash being re-burned is used to ignite more ash). Due to the re-burning technique used by the STAR facility, a special licensing process was necessary to allow for its construction.<sup>4</sup> The LOI content of the ash as it enters the STAR facility ranges from 6 to 10%; the LOI content of the ash after processing is around 0.5%, making it a highly desirable ingredient in ready-mix concrete. Figure 4 shows how installation of the STAR ash beneficiation plant has increased the beneficial use of CCBs from the Morgantown power plant.



## BENEFICIAL USE OF STORED ASH

Many users of CCBs prefer to obtain fresh CCBs directly from power generating stations; indeed, many specifications for fly ash to be used in certain applications call for fresh ash. However, in some situations, beneficial use of ash that has formerly been disposed, either in ponds or landfills, may be necessary. In some parts of North America, the demand for fly ash for use in concrete and other construction materials has begun to exceed the rate at which it is generated at local power stations.<sup>6,7</sup> At first glance, this is a highly attractive beneficial use prospect; in addition to beneficial re-use of what was previously considered a waste material, land formerly used for disposal can be reclaimed, and potential leaching problems associated with landfills can be avoided. Furthermore, manufacturers need not be limited by the rate at which power generators produce and transport ash. However, several factors can cause challenges for the reuse of previously disposed ash.

Of primary concern are the physical and chemical changes that ash can undergo in a storage environment. Class C ash may undergo a decrease in pH as calcium oxide (CaO) is converted to calcium carbonate (CaCO<sub>3</sub>) due to reactions with atmospheric carbon dioxide (CO<sub>2</sub>).<sup>8,9,10,11</sup> Both Class C and Class F ashes may also see the development of secondary minerals, particularly clay minerals that coat or replace the glassy spherical particles that characterize fresh fly ash.<sup>8,10,11</sup> It should be noted that some studies indicate that water is a necessary ingredient for many of these reactions to occur, thus dry-disposed ashes tend to show fewer chemical alterations than wet-disposed ashes.<sup>9</sup>

Landfilled or ponded ash may also be more heterogeneous than fresh ash. Depending upon disposal practices, some parts of the landfill may contain more bottom ash than fly ash, or the two may be comingled. In addition, as burning practices at the power plant(s) using the landfill changed, the characteristics of the ash may have changed as

well. In some projects, pond or fill sites have actually been mapped to identify areas containing the most appropriate CCBs for the desired use.<sup>6,12</sup>

Previously disposed ash may require some reprocessing prior to use as well. Drying is generally necessary for ponded ash. Milling or homogenization may also be necessary in cases of either ponded or landfilled ash.<sup>12</sup>

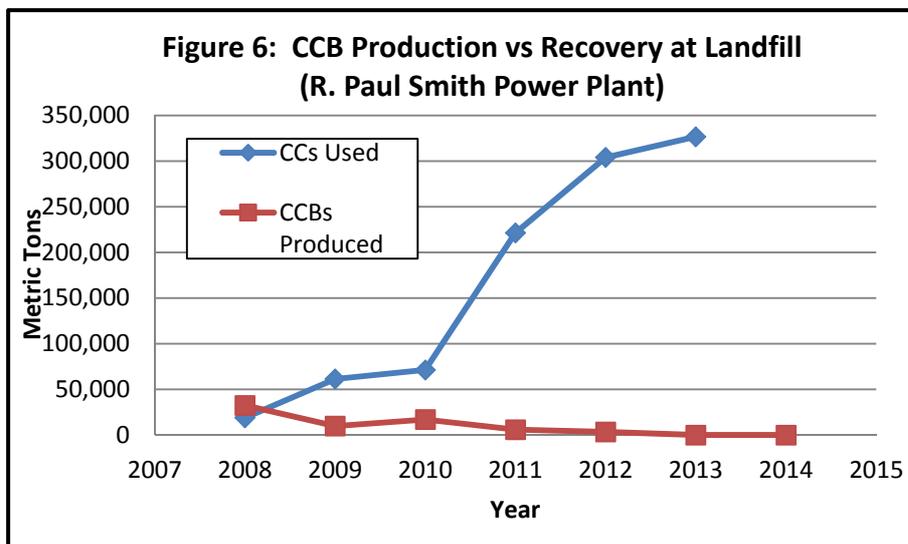
### **Mining of Landfilled Ash from R. Paul Smith Power Plant**

The R. Paul Smith power plant, located in Williamsport, Maryland generated as much as 50,000 tons (45,350 metric tons) of CCBs annually prior to its shutdown in late 2012. The material was conveyed by sluice across the Potomac River to settling ponds in West Virginia. When the CCBs had settled sufficiently, they were transferred to a dry landfill adjacent to the ponds.

Beginning in 2009, in cooperation with local concrete manufacturers in West Virginia, the landfill operators began to excavate ash from the landfill for use in concrete production (Figure 5). During the years 2009 through 2014 (mining of the landfill continued after shutdown of the power plant) more ash was removed from the landfill than was generated at the power plant (Figure 6). At the end of 2014, more than 1.1 million tons (1 million metric tons) of CCBs had been removed from the landfill and beneficially used in concrete production. It is anticipated that the landfill will be entirely mined out by 2020. Once the CCBs have been entirely mined out, the former landfill area will be covered with topsoil and re-vegetated.

**Figure 5: Ash Recovery at R. Paul Smith Landfill**





## OPPORTUNITIES TO FURTHER INCREASE BENEFICIAL USE IN THE FUTURE

Maryland has had great success with beneficial use of Class F fly ash. This is largely due to a thriving concrete manufacturing industry working in concert with the power plants as well as ash beneficiation facilities and landfill mining mentioned above. Maryland also has two power plants which produce alkaline CCBs. The C.P. Crane power plant in Bowleys Quarters, Maryland, began burning sub-bituminous coal and producing Class C ash in 2009. The Warrior Run power plant, constructed in 2000 near Cumberland, Maryland, uses a fluidized bed combustion process. The FBC material is also alkaline and very similar, in nature to Class C ash. The Warrior Run FBC material is utilized in unencapsulated form as backfill for a surface coal mine. The Class C ash from C.P. Crane, however, is landfilled. While tests have been performed to determine whether this ash could be used in concrete manufacture, the ash was found to contain magnesium levels that exceeded those accepted by local concrete manufacturers. Research is currently underway to identify other beneficial use opportunities for both of these materials.

### Mine Grouting Projects

PPRP has successfully demonstrated the potential to use CCBs, particularly alkaline CCBs, to create cementitious grouts suitable for injection into underground mines. Demonstration projects at Winding Ridge and the Kempton Man Shaft.<sup>13,14</sup> Both projects used grouts containing only CCBs and predominantly mine water. At Winding Ridge, the grout was used to fill in a small abandoned underground mine. At the Kempton Man Shaft, the grout was used to create a grout “curtain” surrounding a vertical shaft that allowed shallow water to drain to the deeper mine pool. Demonstration projects like these show that the self-cementing nature of alkaline CCBs, like Class C ash and FBC allows for the creation of injectable cementitious grouts with 100% recycled material and no additional free lime. These grouts can be used to support collapsing tunnels, encapsulate pyritic mine pavement or debris to reduce or

prevent the formation of acid mine drainage (AMD), or may be used to seal tunnels or fractures that operate as conduits that disrupt the natural flow of ground water.

Although CCB grouts have shown great potential for use in the remediation and reclamation of abandoned underground mines, to date, only limited demonstration projects have been performed in Maryland. One factor that limits these types of projects is the lack of an agency at the federal level that focuses on issues related to abandoned underground mines. The federal Mining Safety and Health Administration (MSHA) focuses on conditions within active surface and underground mines. Mine reclamation issues fall under the purview of the federal Office of Surface Mining (OSM), which primarily focuses on surface mine closure and reclamation. While the physical extent of abandoned underground mines may be largely invisible because the mine tunnels lie buried under many meters of rock and soil, these mines have long-term impacts to the environment at the surface via subsidence due to mine tunnel sagging and collapse and the discharge of AMD.

At the state level, the Maryland Department of Natural Resources has an Abandoned Mine Lands Division, which does respond to issues associated with abandoned underground coal mines. In recent years, this agency has been called upon to address issues of ground subsidence affecting highways as well as environmental issues related to AMD discharge. Federal-level support for the reclamation and remediation of inactive and abandoned underground mines could help to support larger scale and more proactive projects, like mine tunnel grouting, across the United States.

### **Carbon Mineralization**

One promising opportunity to beneficially use more alkaline ash lies in the field of carbon dioxide mineralization. Alkaline ashes, like Class C fly ash and FBC material, contain oxides, like CaO and MgO that can react with carbon dioxide in the atmosphere to create carbonate minerals. This process occurs in nature, indeed, the conversion of CaO to CaCO<sub>3</sub> has been noted as one of the weathering reactions that occurs to alkaline fly ashes in landfill environments. However, in nature, this reaction tends to occur very slowly.<sup>15</sup> Research is underway at a number of institutions to find practical and economical ways to speed up this reaction and take advantage of it to capture and sequester a portion of the carbon dioxide from power plant emissions.

A number of different approaches are being researched at the bench scale by various institutions. Many of these processes involve aqueous reactions and chemical additives to catalyze the reaction. Some processes also require the separation of carbon dioxide from the flue gas prior to reacting it with the alkaline ash.<sup>15</sup>

Researchers at the Tallinn University of Technology, in Estonia have performed aqueous CO<sub>2</sub> mineralization using Estonian oil shale wastes (a material that has many similarities to alkaline CCBs).<sup>16</sup> The researchers proposed a pilot-scale system and found that their process could bind up to 290 kilograms of CO<sub>2</sub> per metric ton of ash. Although the aqueous process involved multiple steps, including leaching of CaO from the ash prior to reaction with flue gas CO<sub>2</sub>, no other additives were used in the process,

which was also carried out at atmospheric temperature and pressure. As a secondary benefit, this process produced a highly pure crystalline precipitated calcium carbonate material that could potentially be used by paint, rubber, plastic, or paper industries.

Another research group at the University of Wyoming has published a pilot scale study of a fluidized bed-type reactor that reacts alkaline fly ash with flue gas. Based on the pilot scale study, the researchers estimate that approximately 250 kg of CO<sub>2</sub> could be mineralized onto 1 metric ton of ash.<sup>17</sup> While the amount of CO<sub>2</sub> removed from the flue gas may be modest, the process itself required very little modification to the power plant and demanded very little heat energy to carry the reaction forward, making it a very practicable system.

PPRP has initiated two projects in cooperation with the Frostburg State University (FSU) and the Western Maryland Research and Development Council (RC&D) to study the potential to use alkaline CCBs produced in Maryland to mineralize power plant CO<sub>2</sub> to solid carbonate minerals. Both research groups are working with different mineralization techniques and alkaline FBC material from the Warrior Run power plant. The team at FSU is investigating the influence of pH on mineralization of alkaline ash in an aqueous reaction. The RC&D group is investigating the maximum quantity of CO<sub>2</sub> that could potentially be mineralized by a given quantity of Warrior Run ash.

An additional question to be addressed by research on carbon mineralization is a detailed characterization of the resulting solid materials. While alkaline ash participates in the reaction with carbon dioxide, it is not consumed, and a new by-product stream, with different physical and chemical characteristics from the source material will be produced. While some suggestions have been made for further beneficial uses of this new by-product, none have yet been tested. Some limited leachate testing has been done on these by-products, the results of which suggest that they may be less prone to leaching than alkaline CCBs that have not been used to mineralize CO<sub>2</sub>.<sup>17</sup> PPRP hopes to utilize the recently published Leaching Environmental Framework (LEAF) test methods to shed more light on the potential for this new by-product to leach (or not to leach) constituents in beneficial use applications, particularly stabilized applications.

## **SUMMARY**

Maryland enjoys a high beneficial use rate for the CCBs produced at its seven coal-fired power plants. This success is, in part, due to a thriving concrete industry in the state; however, CCB transformations, both active (in the form of two successful ash beneficiation plants) and passive (in the form of mining previously ponded and landfilled ash) have significantly contributed to Maryland's beneficial use program. In spite of this success, opportunities to further improve Maryland's beneficial use rate remain, specifically in the beneficial use of alkaline CCBs, like the Class C fly ash produced at the C.P. Crane power plant. PPRP has supported successful demonstration projects showcasing the utility of alkaline CCBs to create cementitious grouts for coal mine reclamation. Furthermore, PPRP is currently supporting active research into carbon dioxide mineralization, a process which has the potential to use currently underutilized

alkaline CCBs to reduce the amount of CO<sub>2</sub> released to the atmosphere by coal-fired power plants. Beyond researching the logistics of implementing such a process, PPRP is looking ahead, including partnering arrangements, for beneficial uses for this potential new and distinctive by-product and verification of the leachability of the material in those uses.

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