

Analysis of How Carbon-Based Sorbents Will Impact Fly Ash Utilization and Disposal

Debra F. Pflughoeft-Hassett,¹ David J. Hassett,¹ Tera D. Buckley,¹
Loreal V. Heebink,¹ and John H. Pavlish¹

¹University of North Dakota Energy & Environmental Research Center (EERC)
15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

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ABSTRACT

As more utilities begin to use activated carbon injection (ACI) for mercury control, the potential for the presence of elevated concentrations of mercury, other air toxic elements, and activated carbon (AC) to impact fly ash management needs to be evaluated. Several EERC projects have allowed the collection of comparative baseline fly ash samples and associated fly ash-AC samples from full-scale demonstrations of ACI for mercury emission control. These samples were evaluated for mercury and air toxic element content and mobility and for performance criteria to facilitate a better understanding of the impact of these components in specific utilization applications including use as a mineral admixture in concrete. These data are compared with published data from samples collected at similar large-scale mercury emission control tests.

The data presented are in agreement with previous results from the EERC, the U.S. Environmental Protection Agency, and elsewhere that mercury associated with fly ash is stable and unlikely to be released under most management scenarios.

INTRODUCTION

On March 15, 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule (CAMR) to permanently cap and reduce mercury emissions from coal-fired power plants. This rule makes the United States the first country in the world to regulate mercury emissions from electric generating utilities. CAMR builds on EPA's Clean Air Interstate Rule (CAIR) to create a multipollutant reduction plan for coal-fired power plants. When fully implemented, these rules will reduce U.S. utility emissions of mercury from 48 tons a year to 15 tons, a reduction of nearly 70%.

For many existing coal-fired power plants, the lowest-cost, leading technology to comply with new mercury emission regulations is activated carbon injection (ACI) into the flue gas where the gas-phase mercury can be sorbed on the activated carbon (AC). If the AC is injected upstream of the primary particulate control device (PCD), it will be mixed and collected with the fly ash in the downstream PCDs. In some instances, the AC may be injected after the primary PCD and collected in a separate or secondary downstream

PCD. Both of these ACI strategies will result in an enriched collected fly ash–AC mixture that may need to be managed differently.

The EERC has performed numerous projects related to the utilization and disposal of coal combustion by-products (CCBs) since the 1970s. Recently, the EERC evaluated the impacts of mercury emission control technologies on CCB characteristics and performance to provide information to facilitate appropriate CCB management decisions. The development, testing, and demonstration of mercury emission control technologies have focused on ACI, so as a result, a large number of fly ash–AC samples were evaluated. EERC projects included laboratory-scale evaluations that addressed fundamental issues critical to determining the potential for rerelease of sorbed mercury and other air toxic elements on CCBs under various environmental conditions and settings and evaluation of mercury flux at CCB disposal sites. Using results of recent laboratory studies of mercury release from CCBs and an understanding of CCB management, an analysis of the impact of carbon-based sorbents on CCB management was performed.

BACKGROUND

The U.S. Department of Energy (DOE) and EPA have set goals to increase overall CCB utilization to 50% by 2011. EPA has also set a goal to increase the use of CCBs as a supplementary cementitious material (SCM) in concrete by 50%, from 12.4 million tons in 2001 to 18.6 million tons in 2011, thereby decreasing greenhouse gas emissions from avoided cement manufacturing by approximately 5 million tons. The EPA goal to increase the use of CCBs as SCMs applies primarily to fly ash because nearly 15 million short tons of fly ash are used in the production of concrete and concrete products. In 2005, 21% of the fly ash produced was used in concrete. Other leading applications for fly ash are in structural fills and embankments, as a raw feed for cement clinker production, in waste stabilization and solidification, in soil modification and stabilization, and for mine reclamation.

DOE initiated development of mercury emission control technologies in the early 1990s and, more recently, has conducted multiple full-scale demonstration of promising technologies. ACI is a leading technology undergoing full-scale demonstrations and is expected to be implemented at numerous coal-based electric generating units in order to meet emission standards resulting from current regulatory initiatives. As a result, utility CCB managers and environmental professionals at facilities opting to implement ACI will have a fly ash + AC stream to manage.

PROPERTIES AND PERFORMANCE OF FLY ASH + AC

Properties of fly ash + AC were evaluated under multiple EERC research efforts. The ranges of pH, loss on ignition, and total mercury content of the samples evaluated are shown in Table 1. Fly ash samples without AC present were also evaluated, and comparative data for those samples are also shown in Table 1. In some cases, samples

Table 1. Properties of Fly Ash + AC Samples Evaluated by the EERC

Coal Type	No. of Samples	Sample Type with Hg Control Description	24-hour pH Range	LOI ¹ Range, %	Total Hg Concentration Range, µg/g
Bituminous	21	Fly ash	5.52–12.65	0.47–21.2	<0.01–0.685
	6	Fly ash + AC (post-primary PCD)	3.99–9.20	12.6–24.4	0.742–120
	2	Fly ash + AC (pre-primary PCD)	NT ²	NT	NT
Subbituminous	3	Fly ash	12.27–12.56	0.32–1.08	0.261–1.22
	4	Fly ash + AC (pre-primary PCD)	10.95–11.90	2.28–4.14	1.09–5.81
Lignite	13	Fly ash	10.50–12.74	0.22–7.48	<0.01–0.878
	8	Fly ash + AC (post-primary PCD)	10.52–11.41	0.59–13.2	0.147–64.5
	6	Fly ash + AC (pre-primary PCD)	11.86–12.61	0.96–4.21	0.225–12.7

¹ Loss on ignition.

² Not tested.

acquired included baseline samples (no AC) and test samples (fly ash + AC) from the same facility.

In past work, the EERC has been careful to point out that the LOI of a sample does not directly reflect the carbon content of a fly ash sample. This is true for samples with low LOI values where the carbon present is unburned coal as well as for fly ash + AC samples because there are contributions to LOI that are not related to the presence of carbon. However, the noncarbon contributions are generally very small and, for the purposes of discussion related to fly ash + AC, the LOI value can be used to reflect a comparative amount of AC present.

LABORATORY METHODS

Laboratory methods were used to evaluate the potential for mercury release from fly ash + AC samples. Details of the methods used and developed for this purpose are described elsewhere.¹

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. The leaching tests performed on the samples reported here were the toxicity characteristic leaching procedure (TCLP),² the synthetic groundwater leaching procedure (SGLP), and long-term leaching (LTL) with 30- and 60-day equilibration periods.³ Mercury leachate concentrations were determined using cold-vapor atomic absorption spectroscopy (CVAAS) and cold-vapor atomic fluorescence spectrometry (CVAFS).

A method to evaluate the potential for release of mercury from CCBs at ambient temperatures was developed. The method used 250-mL wide-mouth glass test containers with bonded Teflon liner caps. Two holes were drilled in the caps to accommodate a silicone tube for gas inlet and a Teflon outlet bulkhead fitting. The gas inlet tube extended only slightly into the container, while the outlet tube extended nearly to the bottom of the container. A shorter outlet tube situated above the sample was used for wet flue gas desulfurization (FGD) material samples because air could not flow through the sample to the outlet below the sample surface.

Using these test containers, 75–200-g aliquots of CCB provided a column of material through which the low-mercury air could be transported. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the bottles through a gas distribution manifold to regulate gas flow. Air entering the test bottle passed through the CCB and exited to a mercury collection tube containing two separate gold-coated quartz traps. The trap nearest the exit bulkhead fitting, or analytical trap, collected mercury released from the CCB and bottle. Multiple-day readings were collected, the mercury results from all experimental time segments were combined, and the container blank was subtracted.

To evaluate the mercury release profiles from CCBs exposed to elevated temperatures, an apparatus was constructed to measure mercury release in real time when the sample was exposed to temperatures up to 750°C. As the mercury and mercury compounds desorbed from the CCB in the sample tube, a nitrogen flow carried them to the electrically heated quartz analytical cell (operated at 800°C), allowing the decomposition of mercury compounds to elemental mercury and measurement of all mercury released by atomic absorption spectrophotometry (AAS).

The methods to evaluate microbiologically mediated vapor-phase mercury releases included a sample slurry system which allowed for growth of microbes under aerobic and anaerobic conditions, as introduced by a soil-fly ash mixture with only inherent moisture. Analytical traps were used to capture vapor-phase elemental and organomercury. In some of the slurry experiments, the leachate was also analyzed for total and organomercury.

RESULTS

Leaching results indicated that mercury is not readily leachable from fly ash or fly ash + AC. Most samples had leachate mercury concentrations below the 0.01- $\mu\text{g/L}$ analytical

method reporting limit. Results of short- and long-term leaching for fly ash indicated that total mercury content did not correlate with leachate mercury concentrations. The results indicated that the higher total concentrations of mercury associated with the presence of AC were stable and not readily released through leaching. The laboratory leaching results all indicated that mercury is expected to be stable on CCBs when exposed to water.

Ambient-temperature vapor-phase release experiments indicated that some samples released mercury and some samples sorbed mercury. Sorption was most common for fly ash + AC.

Fly ash samples subjected to elevated temperatures typically generated either one or two mercury peaks, and indicated that mercury were released at temperatures ranging from 256° to 750°C. Some samples continued to show increasing mercury release at 750°C. At this temperature, 100% of the mercury was released regardless of sample type.

In all microbiologically mediated mercury release experiments on fly ash and fly ash + AC, both elemental and organomercury were released at very low levels. Methylation of mercury did predictably occur in the experimental systems, but the apparent rate and resultant concentrations of methylmercury were extremely small.

POTENTIAL IMPACT OF ACI ON CCB DISPOSAL

Currently in the United States, both landfills and surface impoundments are used for CCB disposal; in 2005, an estimated 42 million tons of fly ash was disposed of in these types of facilities. It is too early to estimate the amount of fly ash (+AC) that may require disposal after full implementation of CAMR and CAIR, but an increased volume of fly ash (+AC) may be deemed unsuitable for utilization, and alternate materials that result from ACI and treatment of fly ash + AC may also require disposal. Based on the experiments performed at the EERC and an assessment of information published on EERC and other large-scale mercury emission control projects, the following issues may need to be addressed relative to the collection and disposal of fly ash + AC at utility disposal sites:

- ACI (pre- and post-PCD) may alter the physical behavior of the fly ash (+ AC) and may impact PCD performance. The final fly ash + AC may also exhibit different handling performance such as the level of dusting for dry handling and transport.
- Based on the most recent mercury emission control demonstrations, only a slight increase in material volume is expected if the AC is injected upstream of a primary PCD; however, if AC is injected downstream of the primary PCD and upstream of a secondary PCD, the combined fly ash +AC material will have a significantly higher level of AC.

- Mercury is not expected to be readily mobilized by leaching from CCBs in disposal settings; however, there is higher potential for formation and release of mercury and especially organomercury compounds from wet disposal systems. The amount of mercury release would be expected to be very low.
- Vapor-phase releases of mercury are expected to be extremely low, and the incorporation of AC with fly ash may influence the flux of mercury at fly ash + AC disposal sites to be even more likely to be sorption.
- In laboratory experiments, formation and release of elemental and organomercury was facilitated by the presence of microbial activity and fungus under near-neutral pH conditions, and further evaluation of this phenomenon is required to better understand the impact at CCB disposal sites.

POTENTIAL IMPACT OF ACI ON CCB UTILIZATION

Fly ash + AC generated from systems that inject the AC downstream from the primary PCD are expected to have a much higher AC content than those from systems that inject the AC upstream from the primary PCD. The fly ash collected downstream in the secondary PCD will be fly ash that passed through the primary PCD and will generally be finer in size. Because these materials will be concentrated in AC, they are currently expected to be managed through disposal. The discussion presented is based on information on fly ash + AC samples that were collected from the primary PCD when injecting AC upstream.

Fly Ash Utilization in Concrete

As already noted, the use in concrete is the largest utilization application for fly ash in the United States. Most specifications for fly ash to be used as a mineral admixture in concrete prescribe a limit for the LOI exhibited by the fly ash. LOI is considered by industry to be one of the key quality measures for fly ash but is not necessarily a direct indicator of fly ash performance or carbon content. However, when significant unburned carbon is present in or AC is added to the fly ash, LOI can provide a comparative indicator of the carbon present. Typical LOI limits are 5% or 6%. It is well documented that elevated unburned carbon levels in fly ash impact the use of that material, in part because the fly ash may not meet the LOI specification. The high unburned carbon fly ash may perform well as a mineral admixture in concrete even though it does not meet the existing specification; however, it has also been shown that unburned carbon can be detrimental to the concrete performance when air entraining is required. Air voids in concrete are needed to achieve good performance for concrete exposed to freeze-thaw conditions, and most concrete placed in the United States is air entrained. Air entraining is accomplished by addition of an air-entraining agent (AEA). AEA's can be sorbed onto unburned carbon and AC, making them unavailable to facilitate the incorporation of air bubbles into the concrete mix. Laboratory foam index testing at the EERC and elsewhere has shown that AC, even in very small percentages, can have a drastic effect on the amount of AEA required to produce sustainable foam in cement-fly ash mixtures

which is indicative of performance in real-world concrete production. With the full-scale implementation of ACI for mercury control, the quantity of fly ash that is unsuitable for use as a mineral admixture in concrete is expected to increase significantly.

Based on EERC experiments to evaluate mercury releases from fly ash and fly ash + AC, the potential for mercury to be released from the fly ash in concrete mixing, placement and use is very low. Since the leachability of mercury from fly ash is low, fly ash typically comprises only a small percentage of the entire concrete mix, and the leachability of constituents from concrete is also low, the potential for mercury associated with fly ash to be leached from concrete is very low. The potential for vapor-phase release of mercury is also very low based on ambient-temperature mercury release experimental results. Further the alkaline nature of a concrete mix is not expected to allow for the growth of microbes, so the potential for microbiologically mediated formation and/or release of mercury is low. Laboratory results also can be interpreted to indicate that release of mercury from concrete that is recycled or disposed of in construction landfills should be similarly low.

Geotechnical Applications

For the purposes of this paper, structural fills, embankments, mining applications, and soil stabilization applications have been categorized together as geotechnical applications. Fly ash has properties that are beneficial in geotechnical applications, and the utilization statistics indicated that nearly 7 million tons of fly ash were used for these applications in 2005. For fly ash + AC (pre-PCD), the physical and engineering performance of the material is expected to be similar to that of the associated baseline fly ash, with some potential for handling issues such as increased dusting. The presence of AC is not expected to impact the pozzolanic/cementitious performance of the fly ash. While the specific procedures used to place fly ash for these individual geotechnical applications and to achieve the needed engineering performance, the fly ash used is exposed to similar conditions in the field setting. The conditions will frequently be specific to a site but can be expected to potentially include exposure to moisture or water, ambient temperatures, and contact with soils (either mixing or on a boundary between fly ash and soil). Again, laboratory results indicate that release of mercury through leaching and exposure to ambient temperatures will be very low and should not preclude the use of fly ash +AC in these applications. Neither do results of microbiologically mediate release experiments indicate that mercury will be released in any significant amounts and should not preclude the use of fly ash + AC in these uses.

Cement Manufacture

Fly ash is used as a raw feed for cement clinker production primarily to contribute specific required elements such as aluminum in the final cement composition. When used in this application, the fly ash is exposed to elevated temperatures in the cement kiln. Laboratory experiments used to measure the release of mercury from fly ash when exposed to elevated temperatures indicated that for almost all fly ash and fly ash +AC samples, 100% of the mercury was released from the sample by the time the sample

reached 750°C (1382°F). Since cement kilns reach temperatures significantly higher than the experimental maximum, it is expected that the mercury associated with fly ash +AC would be released during the clinker formation process. This may not mean that all the mercury would be emitted to the atmosphere because the operation of the kiln could result in some of the vapor-phase mercury being captured in existing emission control devices.

On December 8, 2006, EPA issued final amendments to National Emission Standards for Air Toxics (NESHAP): Portland Cement Manufacturing Industry that banned the “use of fly ash from utility boilers if the mercury content of that fly ash has increased as a result of certain utility emission controls (such as activated carbon injection) unless a facility can demonstrate that use of fly ash will not increase its mercury emissions.” EPA also issued a reconsideration of the ban requesting input from industry indicating that the reconsideration would be completed by the end of 2007.

Waste Stabilization and Solidification

A significant quantity of fly ash (2.6 million tons in 2005) was used to stabilize and/or solidify wastes.⁴ American Coal Ash Association statistics do not provide detail on the type of wastes that are stabilized or solidified with fly ash, but long-term experience in working with CCB managers at coal-based power plants indicates that a large amount of the wastes being stabilized with fly ash may, in fact, be wet FGD materials. Wet FGD material (nonoxidized) typically has a high water content and is thixotropic, making it difficult to handle and transport. Wet FGD material is usually disposed of, and in order to stabilize or fixate the material, fly ash is frequently added to produce a more easily managed solid. Fly ash +AC should exhibit similar physical performance in this stabilization process, and mercury releases from direct leaching from exposure to water and direct vapor-phase transport from exposure to ambient air should be small based on laboratory data. However, the use of fly ash +AC to stabilize wet FGD material may provide conditions to promote the microbiologically mediated releases (vapor-phase and leaching) of mercury both from the fly ash +AC and from the wet FGD material which may also contain mercury. Further investigation of the potential for release of mercury from fixated wet FGD materials and FGD materials in general has been recommended by the EERC.⁵

Because of the variety of wastes that may be stabilized or solidified with fly ash, it is not possible to discuss the physical performance or potential mercury release for fly ash +AC except to indicate that the pozzolanic/cementitious performance is not expected to be impacted by the presence of the AC. It is possible that in some waste stabilization applications that the AC may offer some cobenefit because the sorptive capacity of the AC is not expected to be exhausted and could capture waste constituents, enhancing the stabilization effect. This proposed cobenefit would be expected to be small since the amount of AC in fly ash + AC will typically be low.

CONCLUSIONS

Based on results of the laboratory experiments conducted at the EERC and elsewhere, the EERC draws the following conclusions regarding the impact ACI will have on fly ash management:

- ACI will increase carbon and mercury content in fly ash.
- Although the samples had higher total mercury concentration, it is unlikely that mercury will leach from fly ash. It is not expected that regulatory changes will occur for the management of CCBs based on the potential for mercury to leach from CCBs.
- Ambient-temperature release of mercury was low for all fly ash and fly ash + AC materials evaluated in laboratory experiments and is not expected to impact current management practices.
- Mercury was readily released from fly ash and fly ash + AC samples when exposed to elevated temperatures of 750°C and greater.
- The microbiologically mediated release of mercury from fly ash + AC was generally low in laboratory experiments, but organomercury was formed and released consistently under conditions conducive to microbial growth and when fungus was present. Continued work in this area is needed to confirm that mercury releases of this type will not impact current management practices.
- The physical and engineering performance of fly ash + AC is expected to be similar to the baseline fly ash, with the exception that the AC, even at low levels, may preclude the use of fly ash + AC in concrete where air entrainment is specified.

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