

Studies of Mercury Capture on Fly Ash: Examples From Power Plants Burning Kentucky Coals

James C. Hower¹, **Tanaporn Sakulpitakphon**¹, **Darrell N. Taulbee**¹,
and **M. Mercedes Maroto-Valer**²

¹ University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA (859-257-0261; hower@caer.uky.edu)

² The Energy Institute, The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Several studies at Kentucky power plants and at other utilities burning Kentucky coals have demonstrated a relationship between the amount of carbon in the fly ash, the flue gas temperature at the collection point, the form of fly ash carbon, and the amount of mercury captured. Early studies at a plant burning a high volatile C bituminous coal demonstrated a clear increase in Hg capture with an increase in carbon. In the latter case, the fly ash carbons were generally an isotropic coke. At a plant with a more complex mix of fly ash carbons, studies of density-gradient centrifugation fractions showed that Hg capture generally increased from inertinite to isotropic coke to anisotropic coke. Density and BET surface area also increased along the same path. Studies of a plant burning a single-mine source coal suggest that the relationship is much more complex than suggested by early studies. Factors such as the thickness of the carbons and blinding of carbon surfaces by less-adsorbent carbons and inorganics may serve to complicate relationships predicted by chemical and petrographic studies.

INTRODUCTION

The possibility of regulation of Hg emissions from coal-fired power plants guarantees that studies of Hg association and speciation in coals, fly ash, and emissions will continue to be of interest. The Center for Applied Energy Research has conducted a series of studies of Hg in fly ash. Four studies will be briefly discussed below.

PLANT 1: WESTERN KENTUCKY HIGH SULFUR COAL

Hower et al.¹ investigated size fractions of fly ash from a 500-MW unit with a fuel blend dominated by high-sulfur, high volatile C bituminous Western Kentucky coal. ESP fly ash collected at two times during consecutive months was sized at 100, 200, 325, and 500 mesh. Hg was part of a large suite of elements analyzed. The authors found a high correlation between Hg and fly ash carbon (Figure 1). The fly ash carbon was dominated by isotropic coke, which, in comparison to later studies, likely simplified the relationship between the fly ash carbon and the Hg capture.

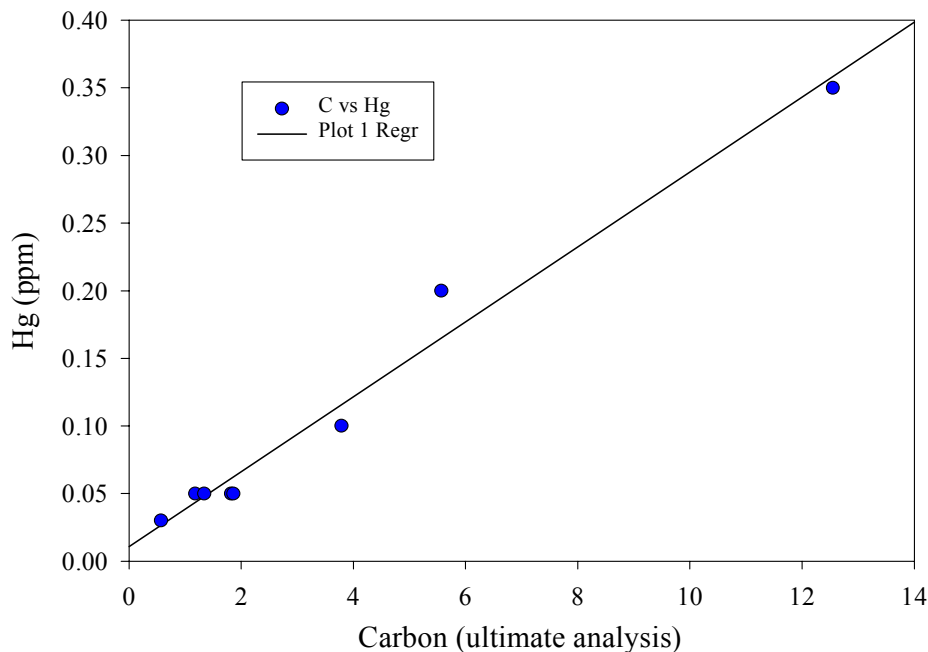


Figure 1. Carbon versus Hg for sized fly ash from a plant burning high sulfur coal.

PLANT 2: CENTRAL APPALACHIAN LOW SULFUR COAL

Hower et al. ² studied a 150-MW plant burning a Central Appalachian low-sulfur, high volatile A bituminous coal blend. The fly ash collection system consists of mechanical collectors followed by a baghouse.

The mechanical collectors tend to capture a higher carbon fly ash than the baghouse. By way of comparison to the previous study, where the fly ash was captured at a single flue gas temperature, the mechanical collectors see a flue gas temperature somewhat higher than the baghouse. The difference could not be quantified in the study, but it is known that the temperature drop across the mechanical collectors is about 190 °C. The relationship between fly ash carbon and Hg capture is, therefore, complicated by the temperature differential between the fly ash types. This is illustrated on Figure 2 where it is seen that the baghouse, while having a lower amount of carbon than the mechanical fly ashes, has a much higher Hg content.

In this particular case, while the fly ash carbons exhibited a greater petrographic complexity than in the previous study, the complexity was more than offset by the temperature difference between the two collection systems.

C vs. Hg

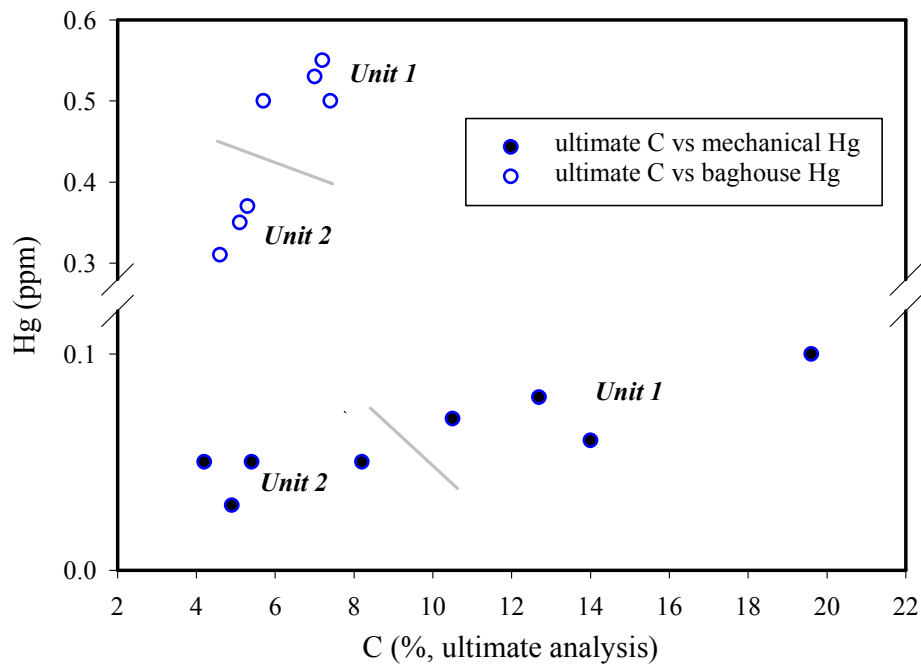


Figure 2. Relationship between carbon (by ultimate analysis) and Hg for different fly ash collection systems in identical units burning Central Appalachian coal. Note break in the Hg scale.

PLANT 3: DENSITY FRACTIONS OF FLY ASH

Fly ash was collected from the mechanical separators of the 70 MW unit 3 at East Kentucky Power's Dale Station.³ Carbon enrichment was accomplished through a screening at 140 mesh (106 μm), followed by triboelectrostatic separation of the +140 mesh fraction obtain a carbon-enriched fraction which was then processed via density gradient centrifugation (DGC) using a lithium heteropolytungstate high-density media. Large-scale DGC separations were conducted with density cut points, as determined by the carbon form concentrations delineated in the preliminary runs, resulting in 17 fractions from $<1.32 \text{ g cm}^{-3}$ to $2.15\text{-}2.30 \text{ g cm}^{-3}$.

Petrographic analyses of the fly ash were performed on epoxy-bound polished pellets using oil-immersion objectives at a final magnification of 500-625x. BET surface area measurements, corrected to a mineral-free basis, were made by N_2 adsorption at 77 $^\circ\text{K}$ on a Coulter Omnisorb model 610. Mercury was analyzed at East Kentucky Power Cooperative's laboratory on a LECO AMA254 Advanced Mercury Analyzer, an adsorption spectrophotometer system.

Eight fly ash samples were analyzed both petrographically and for Hg content and BET surface area measurements were performed on five of the fly ashes. BET surface area

of fly ash carbon forms and Hg content increased from inertinite through isotropic coke to anisotropic coke. This observation differs from a previous study by Hill et al.⁴ which appeared to demonstrate a reverse order for the coke forms in relation to adsorption of air entrainment chemicals. The latter authors used fly ashes from a variety of sources, whereas the use of a single source of fly ash in the present study allowed greater resolution of the contributions of different carbon forms to the BET surface area. None of the fly ashes examined by Hower et al.³ were pure separates of the individual carbon forms owing to the occurrence of mixed phases among the particles within the density fraction.

The basic data for the fly ash separates is given on Table 1 and the summary of the relationships is illustrated on Figure 3.

TABLE 1. Density, Hg content, BET surface area, and fly ash petrography of samples in study by Hower et al.³

Sample	density (g/cm ³)	Hg (ppm)	BET surface area (m ² /g)	dom. carbon	Inertinite	Isotropic coke	Anisotropic coke	Glass
parent		0.138			5.5	24.0	61.0	9.5
2	1.479	0.146	15	inertinite	76.5	7.0	1.0	15.5
5	1.740	0.209	25	isotropic	13.1	72.1	8.7	6.0
6	1.763	0.153	23	isotropic	7.7	65.9	20.9	5.6
7	1.788	0.166		intermediate	3.3	48.4	45.0	3.3
8	1.837	0.140		intermediate	0.0	36.0	62.0	2.0
11	1.912	0.179	35	anisotropic	1.5	22.0	71.0	5.5
12	1.929	0.182	36	anisotropic	0.0	19.5	76.0	4.5

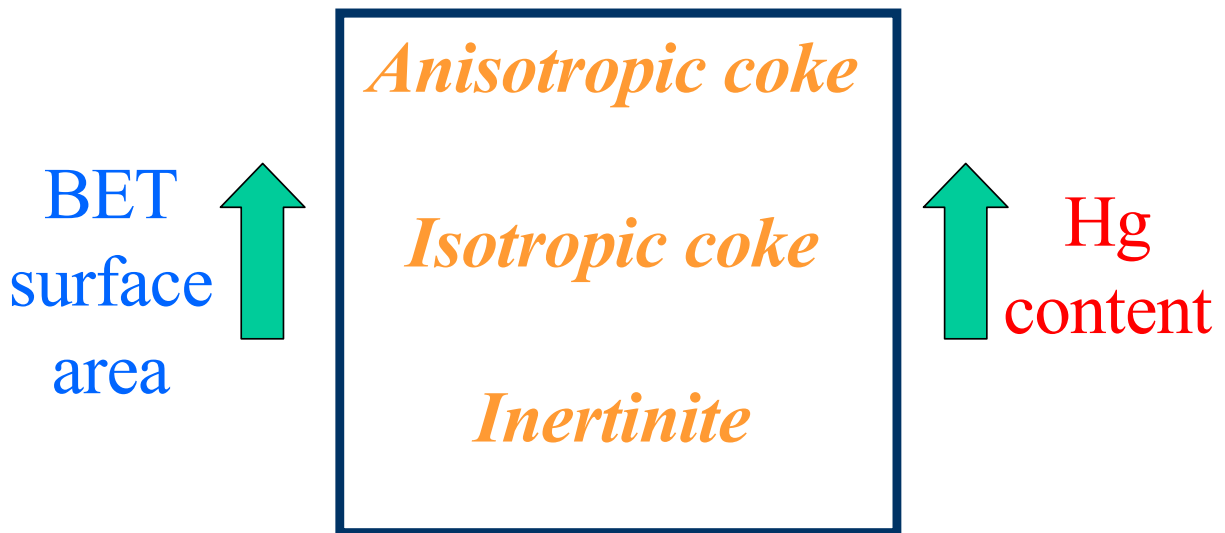


Figure 3. Generalized relationship between BET surface area, Hg content, and fly ash carbon components.

PLANT 4: STUDIES OF THE COMBUSTION OF A HIGH-Hg COAL

Sakulpitakphon et al. ⁵ investigated the combustion of a single-mine coal (Manchester coal bed, Clay County, Kentucky) at East Kentucky Power Cooperative's Cooper Station unit 1 on 19-20 May 1999. Coal and fly ash collection was done on 20 May 1999, at all available points. Fly ash was emptied from the hoppers on at least a daily basis, therefore, fly ash collected on the second day should have been strictly from the single-mine coal feed.

Mercury and petrographic analysis followed the same procedures as the PLANT 3 study, above.

The fuel was a high volatile A bituminous, moderate sulfur coal with a mercury content in excess of 0.2 ppm. Most of the mercury and pyritic sulfur was concentrated in a single lithotype at the top of the coal bed.

Fly ash is collected in two economizer hoppers, four mechanical hoppers, and three rows of two electrostatic precipitators (ESP). The first row of the ESP hoppers was not available for collection. In general, they found the fly ash petrography to be dominated by glass, with glass percentages increasing from the economizers and mechanical hoppers to the ESP, more as a result of the capture of spinel in the first two steps rather than a decrease in carbon forms. Coarser fly ash fractions have greater amounts of carbon. The Hg distribution proved to be asymmetric (Figure 4), with mechanical hoppers 5 and 6 having more Hg, and more carbon, than hoppers 3 and 4. The first

ESP row collected behind hoppers 3 and 4, however, had substantially more Hg than the equivalent hopper behind hoppers 5 and 6.

Hg distribution in fly ash collection

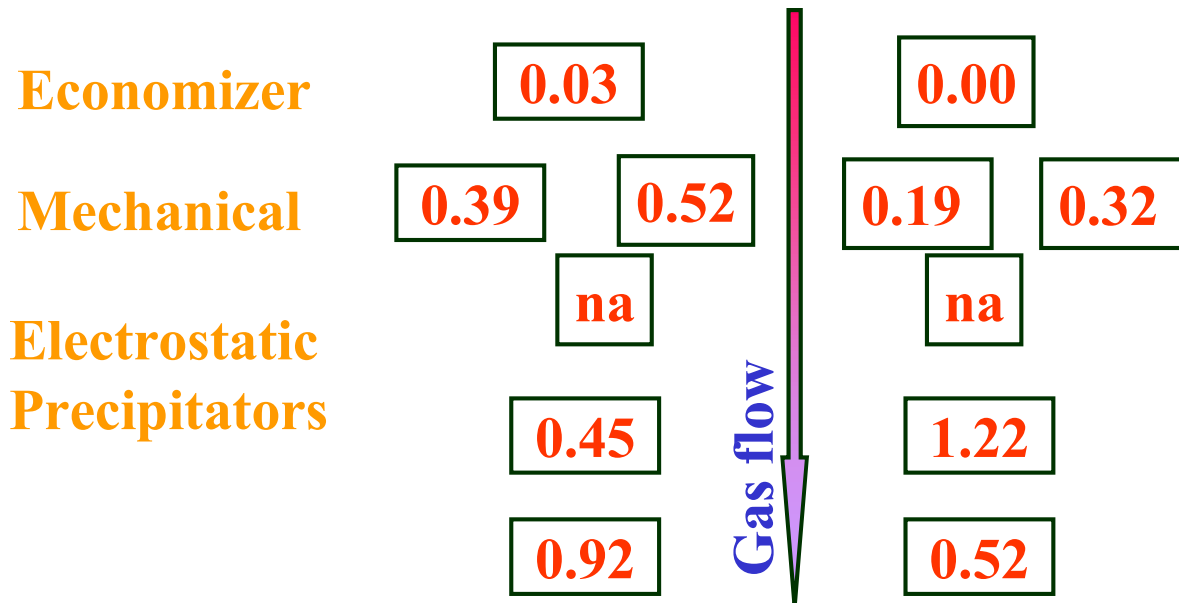


Figure 4. Distribution of Hg (ppm) in the fly ash at Plant 4.

Why is there such a variation in Hg capture between bins, such as the parallel ESP hoppers, which should, in theory, be similar? It is possible that the flue gas on one side of the pollution-control system had a greater Hg content than the other side, leading to the disparity between the mechanical hoppers. Carbon, noted above as a factor in Hg capture, does vary between the hoppers. The form of carbon is also important, as is the position of the carbon relative to the surface of the fly ash particle. The authors noted that the correlation between the carbon form and the carbon actually appearing on the surface of the particle is complex. Any of the carbon particles, particularly the coarser particles, can be a mix of carbon forms. A carbon encased within another form is not going to contribute surface area to the cause of capturing Hg from the flue gas. It will, however, be counted in the chemical and petrographic analyses. Similarly, thick-walled carbons will not have a surface area proportional to their contribution to the chemical and petrographic analyses. Hower and Mastalerz⁶ have proposed a modification of the fly ash classification system used in our previous studies. It is hoped that the more-refined system will provide greater resolution in the correlation of fly ash petrography with fly ash properties.

Blinding of the carbon surface through the deposition of inorganic phases is also possible. The deposition of volatile trace metals, such as As and Pb in the form of

sulfates, would generally be on the surface of glassy particles. Deposition on carbon, however, would complicate Hg adsorption.

CONCLUSIONS

The relationship between fly ash and Hg capture is complicated. While it can be simplified in terms of increasing Hg with a decrease in flue gas temperature in combination with an available substrate, an absorptive fly ash carbon, studies of power plants demonstrate that the reality is not that simple. Further studies of power plants should help to further define the relationships.

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