# The Fate of Ammonia and Mercury in the Carbon Burn-Out (CBO™) Process

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## INTRODUCTION

Carbon Burn-Out (CBO™) has long been known as a very robust system for carbon removal for various types of ash feed stocks. Ash feed stocks with carbon contents ranging from 7% to 90% have been successfully processed.  To date, over one million tons of coal fly ash have been processed using CBO™.

CBO™ processed coal fly ash exhibits excellent pozzolanic activity, consistent air entrainment, consistent LOI at 2.5% or less, and has gained excellent market acceptance.

Recently, there has been much discussion in the fly ash industry about the fate of ammonia and mercury on fly ash.  These two parameters are present in coal fly ash via different mechanisms.  Mercury is inherent to the coal while ammonia originates from post-combustion NOx reduction techniques using ammonia.

Ammonia on fly ash is primarily a result of recent pollution abatement techniques. Coal fired power generation facilities are under increasing pressure for NOx emission reductions.  Recent United States EPA rule changes will require many coal fired utilities to meet NOx emissions limitations of 0.15 lbs./MBTU or less. In order to meet these requirements, many utilities will use a combination of combustion management and post-combustion processes.  Combustion management techniques include low NOx burners, over-fire air systems, gas re-burning technology and flue gas re-circulation.  These methods can contribute to higher residual carbon levels in fly ash, especially when operating for maximum NOx removal.

Post-combustion processes include Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). Use of either of these treatment technologies will result in fly ash contaminated with ammonia slip, which may then be un-marketable, depending on the concentration.

Mercury on the other hand is inherent or naturally occurs in coal.  The average value for fly ash from Bituminous coal combustion is .41 ppm[1].

Given the industry's concerns, Progress Materials recently conducted investigations as to the fate of ammonia and mercury in the Carbon Burn-Out process. This paper presents recent findings concerning ammonia and mercury in the Carbon Burn-Out process.

## THE CARBON BURN-OUT PROCESS

The Carbon Burn-Out process is a thermal process specifically designed for the reduction of carbon in fly ash.

FIGURE  1: <u>CBO™ Process Diagram</u>
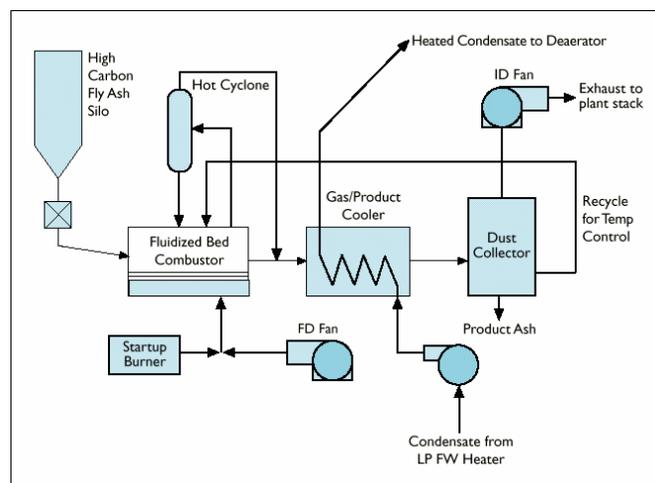


Referring to Figure 1, the CBO™ process flow may be easily summarized:

- High-carbon ash is pneumatically transported to the high carbon fly ash silo.
- FD fan provides fluidization and combustion air to CBO™ fluid bed combustor.
- Start-Up Burner is used only during start up to heat bed to ignition temperature.
- High Carbon feed ash is metered into the combustor.
- Carbon combusts in the FBC on a continuous basis.
- Hot cyclones remove most elutriated particles from FBC flue gas.
- Low carbon fly ash exits FBC via level control weirs.
- Flue gas pneumatically conveys low carbon fly ash, both at about $1300^o$ F through the Gas/Product Cooler.
- In the Gas/Product cooler, heat transfer occurs from hot product ash and hot flue gas to the condensate from the power plant.
- Product ash and flue gas exit at < $300^o$ F.
- Heated condensate returns to power plant's feedwater heater system.

- Product ash is separated from flue gas via cyclone and baghouse.
- ID fan maintains entire CBO™ system at a slight negative pressure, transports product ash through the heat exchanger, and transports cooled, particulate-free flue gas to power plant stack.
- Product ash is pneumatically conveyed to storage for subsequent load out.
- Product ash is also recycled for FBC temperature control.

## AMMONIA AND THE CARBON BURN-OUT PROCESS

Progress Materials' ammonia removal investigation approach was developed to accomplish two primary goals.  The first goal was to determine Carbon Burn-Out's efficiency  in removing ammonia from fly ash.  Data would be generated to determine fly ash ammonia concentrations after Carbon Burn-Out processing.  The second goal was to determine the fate of the ammonia in the Carbon Burn-Out process.  This investigation step involved measuring gas phase ammonia concentrations thereby providing information as to whether the ammonia is exhausted or thermally decomposed within the CBO™ system.

This work on the fate of ammonia in the CBO™ builds on the work previously reported by PMI [2].

### Ammonia Testing Procedures and Results

In order to determine the effectiveness of ammonia removal by Carbon Burn-Out, several fly ash feed stocks of differing ammonia contents were processed.  Processing was accomplished using Progress Materials' one ton per hour pilot facility located in Tampa, Florida.

Ammonia containing fly ash samples from several Eastern United States utilities were selected for processing.  Fly ash ammonia concentrations ranged between 50 and 750 ppmw.  Ammoniated fly ash used in this study was generated in both SCR and SNCR systems.  Ammonia or Urea was used as the process reagent.

Carbon Burn-Out's fluid bed technology provides heat and residence time dictated by conditions for optimal combustion of carbon found in fly ash.  Fly ash residence times of forty-five minutes and temperatures in the 1300°F range are characteristic of the CBO™ process.  Kinetic theory suggest that CBO™ conditions should be ideal for ammonia removal and decomposition.

Both feed and product samples were analyzed for ammonia content.  Ammoniated fly ash was tested by several different methods.  Testing methodology for ammonia in fly ash is not well defined.  However, well-defined methods have been used for solid matrices in environmental testing.  EPA

methods 350.2, 350.3 and a rapid field technique developed by Boral Materials Technologies Inc. were selected for use in our testing program.

Table 1 illustrates results of four different, as-received fly ashes tested using the three methods. EPA methods 350.2 and 350.3 produced similar results. EPA 350.2 uses an aggressive acid distillation step while method 350.3 uses only distilled water for the dissolution of ammonia. The similarity of results between the two methods indicates that the ammonia is water-soluble. The Boral method, which is a simpler-to-run field test, also produced reasonably similar results.

Table1: Ammonia Method Comparison

|  | EPA 350.2 (PPM) | EPA 350.3 (PPM) | Boral Procedure (PPM) |
|---|---|---|---|
| Sample 1 | 300 | 306 | 320 |
| Sample 2 | 351 | 300 | 250 |
| Sample 3 | 534 | 660 | 525 |
| Sample 4 | 735 | 610 | 720 |

Table 2 illustrates ammoniated fly ash samples before and after processing by Carbon Burn-Out. Ammonia content of the feed and product, type of NOx control device used and NOx reagent are shown.

Table 2: Ammonia in Fly Ash Feed

| Feed Ash (PPM) | Product Ash (PPM)* | Control Device | Reagent |
|---|---|---|---|
| 60 | < 5 | SCR | Ammonia |
| 230 | < 5 | SNCR | Ammonia |
| 300 | < 5 | SNCR | Ammonia |
| 500 | < 5 | SNCR | Ammonia |
| 650 | < 5 | SNCR | Ammonia |
| 700 | < 5 | SNCR | Urea |
| 735 | < 5 | SNCR | Urea |

* < Indicates detection limit of the method

Results indicate that under normal Carbon Burn-Out operating conditions essentially all ammonia was removed from the fly ash feed material.

The second goal of the study involved the determination of the fate of released ammonia in the flue gas. To quantify the extent of thermal decomposition of ammonia, flue gas ammonia concentrations were measured at the fluid bed exhaust and the exhaust stack.

The test method selected for ammonia concentration in flue gas was EPA CTM 027, "Procedure for Collection and Analysis of Ammonia in Stationary Sources."

Sampling was conducted after the CBO™ system achieved steady state operation and recycle ash was used for FBC cooling.  Such conditions closely simulate large scale CBO™ operation in the pilot facility.

Results of testing indicate that between 94% and 98% of the ammonia introduced into the system is being thermally decomposed.  That is, the mass of ammonia in the FBC flue gas was between 4% and 8% of that in the feed ash.  Both sampling points produced similar concentrations and decomposition efficiency.


## MERCURY AND THE CARBON BURN-OUT PROCESS

Mercury as a trace element in coal is now coming under increasing investigation, particularly as a contaminant in flue gas from coal-fired power plants.  Technology is being developed to capture mercury (Hg) contained in this flue gas.

Processes that absorb mercury from the flue gas by injecting carbon (typically activated carbon) into the gas ducting show significant promise.  In these processes, the mercury containing carbon may be captured with the fly ash by existing particulate control devices.  These processes report capture rates of up to 90% of the total Hg contained in the coal.  The relatively small amount of carbon used in mercury capture is co-mingled with normally occurring fly ash.

Addition of even very small amounts of activated carbon to fly ash can reduce the value of the fly ash as a pozzolan used in concrete manufacturing.  Activated carbon has been found to interfere greatly with the air entrainment reagents used in concrete mix designs[3].

While most of the regulatory effort has been on removing mercury from flue gas, the presence of mercury on either fly ash or on mixtures of fly ash and activated carbon slated for disposal is of significant concern.  This scenario has the potential to change once marketable fly ash into a solid waste.

It was clear that the CBO™ process would combust the small amounts of activated carbon, along with the carbon in the co-mingled ash, and that the mercury would be vaporized at the FBC temperature.  What was not clear was what the final fate of that mercury would be.  One possibility was that it could simply remain in the vapor state and exit the CBO process in the flue gas.  However, since the flue gas is cooled in the G/P Cooler, another possibility was that some fraction of the mercury would condense on the product fly ash and become sequestered when the fly ash was bound in the concrete matrix.

**Mercury Testing Procedures and Results**

A testing program was designed to determine the fate of mercury in the CBO™ process. A commercial scale CBO™ system was used for this testing program. Fly ash processed in this study was from a utility boiler without activated carbon mercury control equipment so the mercury represents only that captured by the fly ash. Various studies indicate that this can represent 30% to 100% of the total mercury from the coal. [4,5]

Table 3 illustrates sampling points used in this program, sample matrix and the sample type

Table 3: <u>Mercury Sampling Locations</u>

| Sampling Point | Matrix | Sample Type |
|---|---|---|
| Fly Ash Feed | Solid | Grab |
| Fly ash product | Solid | Grab |
| Fluid Bed | Solid | Grab |
| Hot cyclone Inlet | Gas, Solid | Ontario Hydro |
| Hot Cyclone Outlet | Gas, Solid | Ontario Hydro |
| Baghouse Inlet | Gas, Solid | Ontario Hydro |
| Baghouse Exhaust | Gas, Solid | Ontario Hydro |

A mercury balance of the CBO™ process was constructed by examining the mercury concentration of the high carbon feed, low carbon CBO™ product and the exhaust gas of the CBO™ system.

Table 4 illustrates the results of this approach. Three separate runs were used to determine the CBO™ system mass balance for mercury. The data shows excellent mass balance recovery ranging from a low of 94% to a high value of 109% with the average being 101%.

As the data indicates, virtually all of the mercury entering the CBO™ system on the high carbon fly ash feed is found on the low carbon fly ash product. Only .02% of the total mercury entering the CBO™ process is found in the exhaust gas of the system. The remaining 99.98% of the mercury entering the CBO™ process on the high carbon fly ash exits the system with the low carbon CBO™ fly ash product.

Table 4: Mercury Mass Balance for CBO™ Process

| Run | Hg-Feed Mg/hr | Hg-Product Mg/hr | Hg-BHO Mg/hr | Prod+BHO Mg/hr | Material Balance % |
|---|---|---|---|---|---|
| 1 | 13159 | 12395 | 12 | 12407 | 94 |
| 2 | 9899 | 9778 | 19 | 9797 | 99 |
| 3 | 11193 | 12119 | 37 | 12156 | 109 |
| Average | | | | | 101 |

Considering the operational temperatures of the CBO™ process, normally in the 1300° F range, one would assume that mercury would volatize and might exit the CBO™ process in the vapor phase. Indeed, fly ash samples taken from the fluid bed contain essentially no mercury. However, the mass balance information presented in table 4 does not support the assumption that mercury exits the CBO™ system along with the flue gas since virtually all the mercury introduced into the process exits "particulate bound" with the low carbon CBO™ product material.

Mass balance information in table 4 suggests that mercury volatization and a subsequent absorption/adsorption process is taking place within the CBO™ process. In order to develop an understanding of this mechanism speciation data was examined from several Carbon Burn-Out sampling points.

Table 5: Mercury Particulate/Gas Data

| Sampling Point | Matrix | Sample Type | Particulate | -------Vapor Phase----- Oxidized | Elemental |
|---|---|---|---|---|---|
| Fly Ash Feed | Solid | Grab | 100% | | |
| Fluid Bed | Solid | Grab | | >96% | |
| Hot Cyclone Inlet | Gas, Solid | Ontario Hydro | | >96% | |
| Hot Cyclone Outlet | Gas, Solid | Ontario Hydro | | >96% | |
| Baghouse Inlet | Gas, Solid | Ontario Hydro | 99.7% | .2% | .1% |
| Fly Ash Product | Solid | Grab | 100% | | |

Combining the results presented in Table 5 with the CBO™ process diagram (figure 1) the fate of mercury in the Carbon Burn-Out Process becomes clear. Mercury enters the CBO™ process in the high carbon feed material. Mercury contained with the feed is on the particles of the fly ash.

The fly ash is then metered into the fluid bed combustor and subject to temperatures in the 1300°F range and residence times approaching 45 minutes. In the fluid bed combustor, the mercury is volatized and exits the fluid bed in the vapor state, existing as either the oxidized or elemental form.

The mercury free, low carbon fly ash product exiting the fluid bed is combined with 1200°F to 1300°F flue gas from the hot cyclone. At this point in the process, the hot cyclone exhaust gas contains essentially all of the mercury.

The combined stream of mercury laden flue gas from the hot cyclone discharge and mercury free fly ash exiting the fluid bed enter the gas/product cooler. The combined stream is then cooled from 1100°F to 300°F and subsequently collected by the cold cyclone and baghouse for storage or shipment.

The speciation data shows that fly ash efficiently captures the mercury as the hot fly ash and gas stream pass through the gas product cooler and cold cyclone. By the time the gas stream enters the baghouse, the final particle collection device of the CBO™ process, mercury is particulate bound.

Fly ash enters the gas/product cooler virtually mercury free and by the time it exits the low temperature cyclone, the mercury that was entrained in the flue gas is efficiently transfered to the fly ash. The conditions associated with the G/P cooler and cold cyclone are ideal for the capture of mercury.

The conditions associated with the G/P cooler and cold cyclone are as follows:

Table 6: G/P Cooler & Cold Cyclone Conditions

|  | G/P Cooler Inlet | Cold Cyclone Discharge |
|---|---|---|
| Fly Ash Carbon Content | 2% | 2% |
| Fly Ash Mass Flow | 60 TPH | 60 TPH |
| Flow Rate | 13,500 DSCFM | 13,500 DSCFM |
| Temperature | 1050°F | 300°F |
| Residence Time | 1 sec | 3-4 sec |

## CONCLUSIONS

Mercury and ammonia are two environmental parameters of interest for the fly ash industry. Progress Materials has undertaken in-depth studies to determine the fate of ammonia and mercury in the Carbon Burn-Out system.

Results indicate that, under normal Carbon Burn-Out operating conditions, essentially all ammonia is eliminated from the fly ash feed material and

decomposed.  Fly ash having ammonia concentrations between 300 and 750 ppm were processed and in all cases the Carbon Burn-Out process successfully reduced ammonia concentrations below detectable levels.  The Carbon Burn-Out process with operational temperatures at 1300°F and 45-minute solid residence times decomposes the ammonia associated with the fly ash.  Thus ammonia air emissions tests found that all but 4% to 8% of the total ammonia from the feed ash was decomposed.

Mercury is inherent to coal combustion and, even without activated carbon injection for mercury capture, a substantial portion of mercury found in the coal remains with the high carbon fly ash used as feed for the Carbon Burn-Out system.  Operating conditions of the Carbon Burn-Out process results in mercury being volatized and subsequently absorbed/adsorbed on the fly ash product.  Process efficiency for the absorption/adsorption process approaches 100%.  Therefore, essentially all of the mercury entering the CBO™ process exits the process attached to the product ash.  The product ash is used in concrete so the mercury becomes sequestered in the concrete product.

Testing conditions presented in this paper were conducted on Carbon Burn-Out systems functioning in their normal operational modes.  No additional equipment modifications or process changes were made .

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