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On-Line LOI Analyzers for NO_x and Mercury Control

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Abstract:

Concerns about bioaccumulation of mercury (Hg) in the food chain have led to a decision to regulate Hg emissions from US coal-fired power plants. Recent tests sponsored by the US Department of Energy and led by ADA-ES have shown that powdered activated carbon (PAC) can remove a significant fraction of the Hg at flue gas temperatures below about 325 °F. Fly ash carbon, although lacking the capacity for Hg that PAC contains, can also absorb significant Hg under certain conditions. These conditions include low flue gas temperature, adequate chloride content of the coal (bituminous only), and enough contacting time available upstream of and within the particulate control device. How much Hg that might be absorbed is sometimes influenced by the amount of carbon in the flyash up to a level of about 15-30%, and the Hg concentration of the flue gas.

On-line LOI analysis has been used to correlate Hg reduction with changes in fly ash LOI. Test results can be used to plan a **low-cost Hg control strategy** that maximizes the inherent capture and minimizes capital costs and operating expenses. This paper describes a system in which combustion modifications are used to control LOI at about 10-20 percent in order to capture 50-60% of the Hg. If and when additional Hg removal is required, it could be accomplished by PAC injection (only when necessary). Carbon separation technology is then used to produce a salable ash stream at 4 percent carbon, and a disposable or reusable carbon-rich stream containing most of the Hg.

Introduction:

In utility boilers firing coal, very small amounts of the fuel carbon pass through the boiler without being combusted, irrespective of the process conditions or the coal type. To put this in perspective, if a 10-percent ash coal (dry basis) burns to 99% completion, the unburned carbon content of the fly ash will be 9.1 %. If burnout is 99.5%, the unburned carbon is 4.8% of the fly ash. However, the difference between 99% and 99.5% burnout is the difference between selling the ash for revenues and landfilling the ash at some expense. All of the unburned material is entrained in the flue gas, and most is subsequently captured along with the mineral ash in the dust collectors.

Evidence suggests that the unburned carbon does not bypass the combustion zone unreacted, but instead undergoes considerable changes depending on the design and operation of the boiler and the combustion system. In particular, conditions that limit NO_x formation also tend to increase the carbon content of the ash. This paper summarizes how carbon residues can be affected by low- NO_x combustion systems and how some plants may be able to take advantage of unburned carbon to limit Mercury emissions.

Motivation:

Unburned carbon levels in the flue gas have a significant impact on the cost of generating electricity in a power plant. Impacts include:

- Boiler efficiency and heat rate.
- Dust collection efficiency of the electrostatic precipitator.
- Value of the fly ash as a salable byproduct.

Additional impacts may be emerging as multi-pollutant emission-control systems are implemented in the near future. In particular, unburned carbon can absorb mercury at typical air heater outlet gas temperatures, given enough time at the appropriate temperature. Since unburned carbon absorption capacity is very limited, the available carbon surface area also determines the amount of Hg absorbed. Therefore, it may be possible to design and operate a combustion system to optimize unburned carbon for NO_x and Hg control, and use carbon separation technologies for Hg recovery and to produce salable ash.

Carbon residues from coal flames:

Coal is a heterogeneous compound consisting largely of partially decomposed and compressed plant materials from prehistoric times. Differences in plant materials, the extent of decay, and the temperature and pressure exerted on the materials by nature all affect coal combustion properties. The process of converting plants to coal is called “coalification”. Coal burned in US power plants ranges in rank from lignite (where the plant material is still recognizable) to bituminous (which tends to be more dense, brittle, and compacted, and the plant material shows up as bright and dark bands). Coal composition and hardness play a role in understanding unburned carbon.

Coal is pulverized prior to combustion in most boilers. Burner suppliers in the past have specified that the coal must be 99% smaller than 50-mesh (300 microns), and 70% smaller than 200-mesh (74 microns) in order to provide acceptable ignition and burnout. These specifications are no longer applicable for low- NO_x combustion, but the pulverizers are generally too expensive to upgrade during a low- NO_x retrofit.

Figure 1 shows the steps in coal combustion.

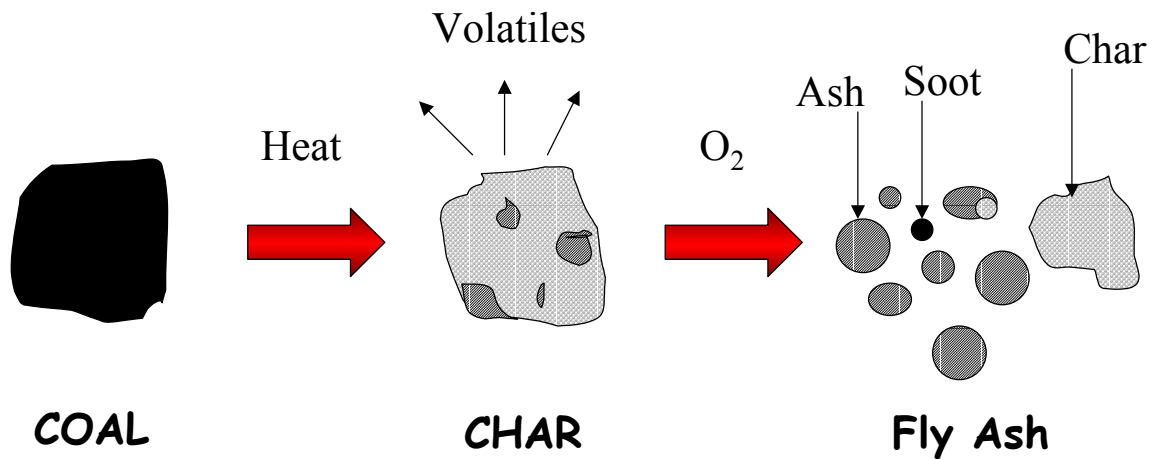


Figure 1. Coal Combustion

As soon as the coal enters the hot furnace environment it begins to decompose, and volatile gases evolve and burn leaving behind a porous solid residue called char. Coal minerals (ash) mostly remain with the char during devolatilization and initial combustion. From 50 to 80% of the coal becomes volatile at typical furnace temperatures (much more than ASTM volatile analysis yields because the ASTM test is done at much lower heat-up rates).

The char formation process for bituminous coals is very different from that of sub-bituminous and lignite coals. Bituminous coals go through a plastic (coal tar) phase as chemical bonds rearrange during devolatilization. Some coking bituminous coals may expand like tiny balloons as volatile gases get trapped in the tar, leaving behind a sponge-like char structure. This kind of a char structure has lots of internal surface area and therefore should burn quickly. In old high-NO_x combustion systems it did burn quickly. However, recent work has revealed that rearranging the chemical bonds under reducing conditions (created by some low-NO_x burners and all staged combustion systems) produces more graphitic crystal formation. This has a double-whammy impact on unburned carbon: the start of carbon burnout is delayed because the plastic phase persists, and the carbon residue is less reactive with oxygen later in the furnace.

Sub-bituminous and lignite coals do not experience a plastic phase during devolatilization, and the coal structure is not changed as much when char is formed. In general, they produce less char and more volatiles than most bituminous coals, but the volatiles contain fewer combustibles and more CO₂ and water vapor. In general, char from these coals burns freely as long as there is any oxygen around. When unburned carbon does occur with sub-bituminous coals, the cause is usually related to delayed ignition and subsequent flame impingement on cold furnace walls due to not adjusting the burners for the poor combustion quality of the volatiles.

After the volatiles start to burn, the char ignites too. The rate of char combustion is initially controlled by the amount of oxygen in contact with the coal. Oxygen is usually

limited in low-NO_x flames (a major factor in unburned carbon formation) so most of the char burnout happens in the post-flame region of the furnace. In the post-flame region, burnout is controlled by diffusion of oxygen to the char surface as well as the amount of time at temperature before quenching and the reactivity of the char. Particle quenching happens when either the char particle hits a cold furnace tube surface, or enters the convective pass where gas temperature falls rapidly.

Figure 1 shows several forms of carbon that have been identified in fly ash samples using microscopy techniques. Char particles can be either amorphous or graphitic. Amorphous particles are porous and spongy, and often have irregular shapes. They are fairly similar in structure to the raw coal except that there is no volatile matter left in them. Graphitic char is usually smooth and rounded. Chemical reactions that take place during Devolatilization leaves these particles with less porosity and reactivity. Some carbon in the ash is attached to the inorganic fly ash particles. This carbon can be either amorphous or graphitic. Soot particles are very rare, but can occur during low-NO_x combustion. They are much smaller than residual carbon particles, and are formed when coal volatiles do not have sufficient air to burn.

Factors that affect unburned carbon:

These factors can be categorized as fuel effects, burner/furnace design effects, or equipment operating effects. Keep in mind that the coal char always starts to burn. In fact, typically more than 98% of the char will burn. These factors all address the question of **why some of the char stops burning.**

As discussed above, coal properties affect char formation. Coal grindability is important because it determines coal pulverizer performance (throughput and size distribution of the pulverized product). Larger (> 100 microns) particles take more time to heat up, devolatilize, and burn. Therefore, this size fraction is harder to ignite, produces more graphitic crystals under low-NO_x conditions, and requires a larger furnace to prevent quenching.

Burner designers also look at the fuel ratio: defined as the ratio of ASTM fixed carbon to volatiles. The higher this ratio becomes, the harder a fuel is to ignite and the more char must be burned. A low-NO_x burner must be set up to provide faster initial mixing for such coals, so NO_x emissions also tend to be higher.

Char structure, as discussed above, is very important. The tendency of different coals to produce unreactive chars can be related to coking parameters. For example, some designers look at Free Swelling Index (FSI) as an indicator for high-unburned carbon. Another factor is the oxygen reactivity of the char, which is determined by porosity, surface area, and density of reactive sites in the char. Some researchers believe that these properties can be deduced from reflectance tests, which categorize the coal based on the amount of specific kinds of plant remnants found in the coal.

The design of the furnace and the combustion system sets the boundary conditions for combustion and char burnout. Combustion rates are simply a function of time, temperature, and oxygen availability as set by the design. Table 1 summarizes some of the important design factors that influence unburned carbon.

Design Factor	Typical Range	Impact on Unburned Carbon
Burner Spacing. This factor is usually measured in terms of Burner Zone Heat Release defined as the total heat input to the burners divided by the amount of boiler tube surface area ten feet above and below the burners.	100,000 to 500,000 Btu/h-ft ²	Tight horizontal and vertical burner spacing produces higher flame temperature. Higher flame temperature increases volatile yield, char reactivity, and initial rate of burnout.
Furnace Height. Determines the amount of time available for carbon burnout.	10 to 60 feet (0.3 to 2.0 seconds)	The mean, bulk-gas residence time above the top row of burners (or OFA ports) should be at least 1 second to prevent increased unburned carbon with low-NO _x combustion.
Furnace Exit Gas Temperature (FEGT). This is gas temperature entering the convective pass, after which char combustion stops.	1900 to 2600 °F	High upper furnace temperature increases burnout, but in most boilers high FEGT comes at the expense of short residence time.
Furnace Cross-Section. Determines the probability of flame impingement on water wall surfaces.	Varies with burner type. Measured as ratio of burner throat diameter to distance to wall.	Flame impingement stops or delays char combustion.
Fan Limitations. Increased pressure drop or air leakage can cause low excess air at the burners. Can be caused by convective pass fouling, adding downstream emission controls (SCR reactor), or boiler age (in the case of leaks).	Depends on unit.	Operators rely on accurate flue gas O ₂ measurement for combustion control. Insufficient airflow to the burners or OFA ports will result in more unburned carbon.
Excess mill capacity. Allows an operator to increase mill fineness when unburned carbon is high.	Varies with mill type and coal properties.	Mills can produce finer coal by sacrificing capacity. Going from 75% to 90% through 200-mesh can cut unburned carbon in half.

Furnace type (wall-fired, tangentially fired, arch-fired) has very little impact on the amount of unburned carbon produced by a particular boiler firing pulverized coal. Cyclone-fired boilers are a separate case. These boilers fire crushed coal (4-mesh or 1/4-inch top size) instead of pulverized coal. Most of the coal is designed to burn when trapped in a layer of slag that coats the inside walls of the combustor. Unburned carbon from cyclones is therefore related to the amount of coal that escapes the combustor and must then burn in suspension in the main furnace. Factors such as slag viscosity and furnace temperature usually determine where the coal burns, and therefore how much carbon is contained in the fly ash. For most coals, the unburned carbon is less than five percent, but can be as high as 30-60% when low sulfur, low iron, high moisture fuels are burned.

Operation and maintenance of the boiler and combustion system also affects the amount of unburned-carbon residue in the fly ash. Coal fineness can be improved (slightly) by reducing primary airflow, tightening classifier settings, or in some cases by adjusting grinding zone gaps or spring tension. Unbalanced coal flow to individual burners can also cause some burners to operate too fuel-rich, increasing the carbon residue from those flames. Similarly, secondary air maldistribution is a problem for some boilers. Balancing coal and airflows to individual burners is a way to reduce unburned carbon without increasing NO_x emissions. Increasing excess air will consume more carbon, but also increase NO_x emissions.

How Low-NO_x Combustion Systems Affect Unburned Carbon:

By 2004, almost every coal-fired utility boiler will have installed some sort of low-NO_x combustion equipment. Low-NO_x burners are applicable to all boilers except cyclone-fired boilers. These burners differ in design details, but all of them create fuel-rich regions within the flame where NO_x formation is prevented and/or NO_x formed in the ignition zone is destroyed. In some boilers, low-NO_x burners are used in combination with Overfire Air (OFA) Ports. For these units, the reducing regions in the flames are more fuel-rich, and char burnout is delayed until the OFA is added into the upper furnace. Therefore, time for carbon burnout is reduced by 0.5 to 1 second when OFA is used. Also, peak flame temperatures are lower during low NO_x firing because fuel heat is released more slowly over a larger portion of the furnace volume.

So, how do these rather significant changes affect fuel combustion chemistry and transport relative to carbon burnout? First coal devolatilization changes. Temperature is slightly lower, less oxygen is available to combust the volatiles as they are released, and the time over which char is formed is longer. All these factors contribute to more crystalline carbon and less amorphous carbon in the char. Reducing conditions also can produce a carbon form not found in high-NO_x flames: soot. Soot consists of micron-sized hydrocarbon solids produced from the coal volatile matter. Volatiles are highly reactive. When there is not enough air to burn the volatiles, they will react with themselves (in a two-step process called “cracking” followed by polymerization) to

produce larger molecules that are condensed as the flame cools. Once formed (at temperatures below 2400 °F), soot is not very reactive with oxygen, so burnout is unlikely before these particles enter the convective pass.

As mentioned above, bituminous char structure also changes when coal devolatilization occurs under reducing conditions. The time where the coal is “plastic” can be greatly increased. During this time, molecules are more mobile and chemical bonds can align into ordered crystals. More graphitic char and less porous (amorphous) chars are produced. Also in the fuel rich flame regions, there is a competition between volatile matter and char for the limited amount of available oxygen. The volatile matter will always prevail because gas-phase combustion is so much faster than heterogeneous combustion. Remember that the true volatile release for many coals can be as high as 80 percent, so local oxygen concentrations could be very low when char finally starts to burn.

Flames are longer for low-NO_x combustion, and coal particles are more concentrated in the center of the flame. If the flame is long enough to impinge on the opposite furnace wall, particle burnout will be even further delayed. Post flame temperatures can be lower in some low-NO_x combustion systems. Marginal coal particles, (that is, those that are just small enough to be burned under normal conditions) will probably exit the furnace with more carbon left unburned.

Generally speaking, unburned carbon increases as NO_x emissions decrease. For example, at one plant, going from 0.7 lb./MBtu to 0.4 lb./MBtu (via low-NO_x burners) increased the unburned carbon content of the fly ash from 5 percent to 10 percent. When OFA ports were opened all the way, NO_x decreased to 0.3 lb./MBtu, but unburned carbon also increased to 20 percent.

Using Online LOI for Hg Control:

The influence of flyash LOI on mercury (Hg) emissions was measured by ADA-ES at Salem Harbor Station¹. On Wednesday, September 25, 2002 in the late night hours, Unit 1 boiler load was decreased from ~85 MW to ~65 MW. This boiler load decrease and a slight adjustment to the excess air appeared to drop LOI levels from mid 30% range to approximately 20%, based on the CAMRAC on-line LOI analyzer. This change in operating conditions increased the vapor phase mercury concentrations at both the inlet and outlet locations. Coal variability contributed to the increase in uncontrolled Hg level.

The following night between the hours of 19:30 – 06:00 the effects of combining increased flue gas temperature with a reduced LOI condition were evaluated. At 19:30, the steam coils were placed into service, and ESP inlet temperatures were increased approximately 40-50°F to an operating temperature range of 310-320°F at the ESP inlet. Unit 1 operated at this increased temperature condition for a period of 2 ½ hours. During this time, vapor phase mercury concentrations appeared to increase at both the inlet and outlet of the ESP as measured by the Hg S-CEMs.

After operating at that condition for 2 ½ hours, the decision was made to reduce load from 85 MW to 65 MW and operate at the lower LOI condition with the steam coils still in service. LOI dropped from about 35% to about 20%, per the LOI analyzer. Once again, an increase in vapor phase mercury concentrations was observed at both the inlet and outlet locations. This may be important to Salem Harbor and other sites in setting process conditions appropriate to meet future mercury emission limits.

During these test conditions (lower LOI and increased temperature), Hg concentrations increased from 2-4 $\mu\text{g}/\text{Nm}^3$ to approximately 8 $\mu\text{g}/\text{Nm}^3$ at the inlet location. Data from the Hg S-CEMs also indicates an increase at the outlet location. The physical location of these measurement locations can be seen in Figure 2 (for data reported herein, locations #1 (ESP inlet) and #3 (ESP outlet) were used).

Salem Harbor – Sampling Locations

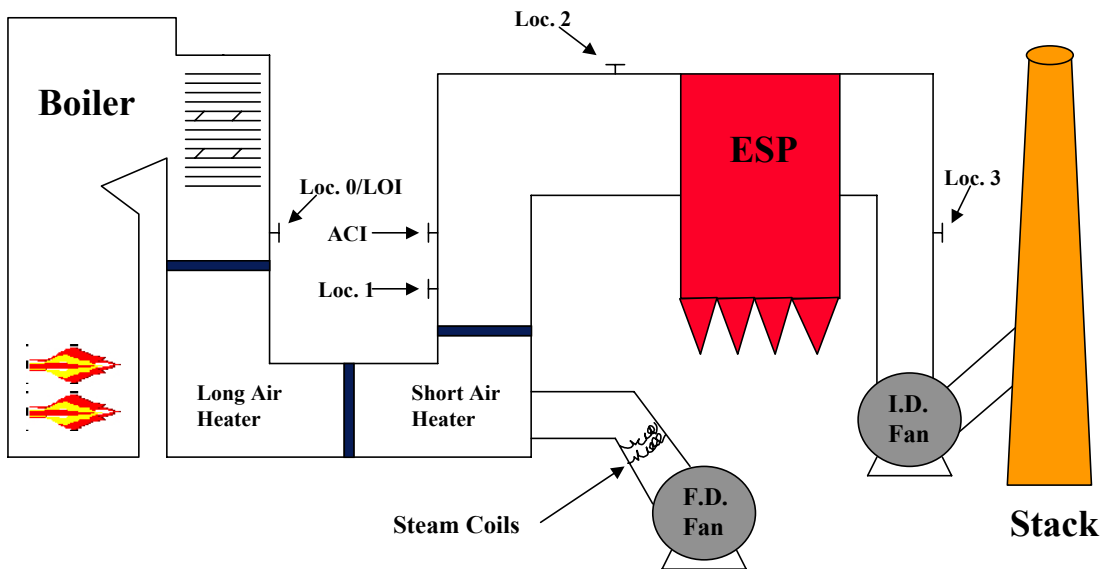


Figure 2. Sampling Locations at Salem Harbor #1

Figure 3 shows how LOI varied with load over these two days. Although there are some fluctuations evident from individual data points (each accumulated over a 20-30 minute period), the trend toward lower LOI at lower load is clear. Figure 4 shows LOI variation over time during the test period.

LOI as a Function of Load at Salem Harbor #1

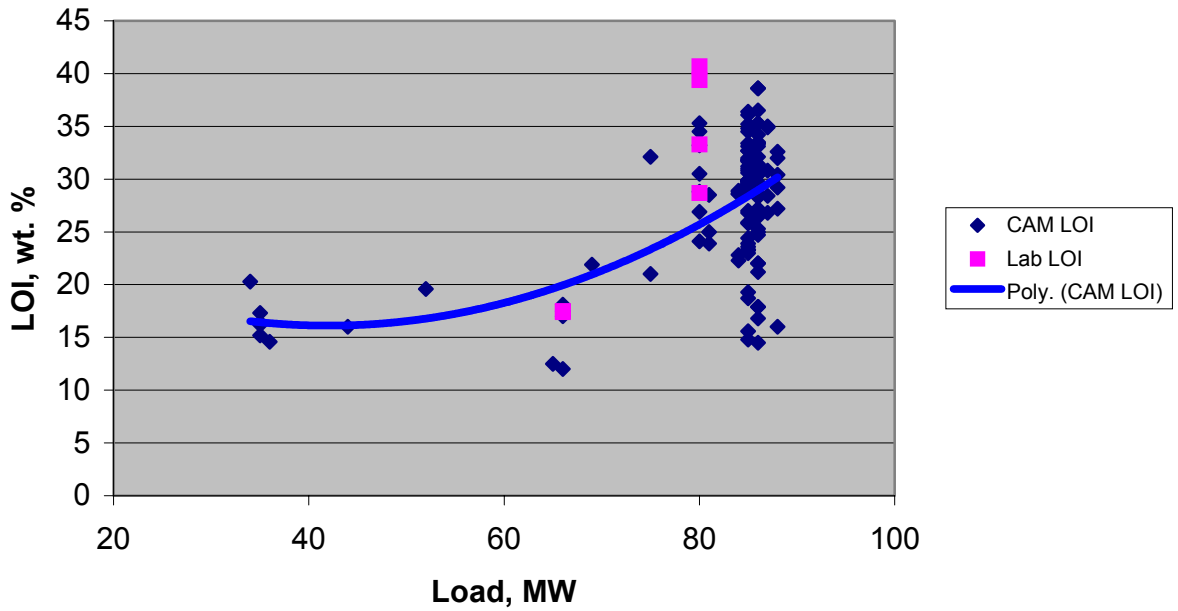


Figure 3. LOI as a Function of Load at Salem Harbor #1

LOI Trend at Salem Harbor #1 on 26 September 2002

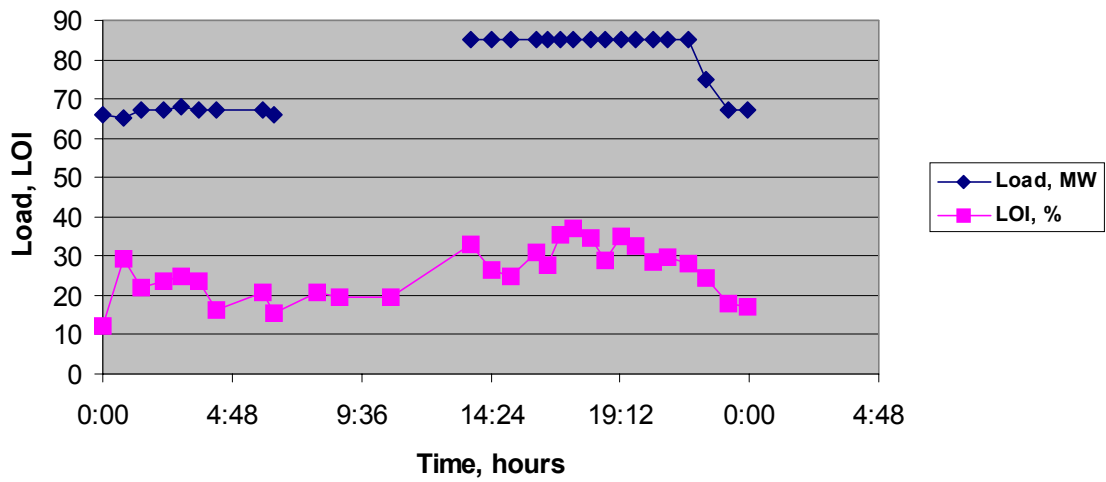


Figure 4. Load and LOI Trends during Hg Tests

The Hg removal results are shown on Figures 5 and 6. Figure 5 shows a very strong correlation between the precipitator inlet temperature and Hg capture for this coal. Hg removal falls off considerably when the temperature rises above 310 °F. Conversely, Hg capture can be up to 90% when the precipitator inlet temperature falls below 270 °F, as it normally does for this boiler. The implication is that boilers with sufficiently low ESP inlet temperatures can take advantage of the LOI for Hg capture, **as long as they have a reliable way to control LOI.**

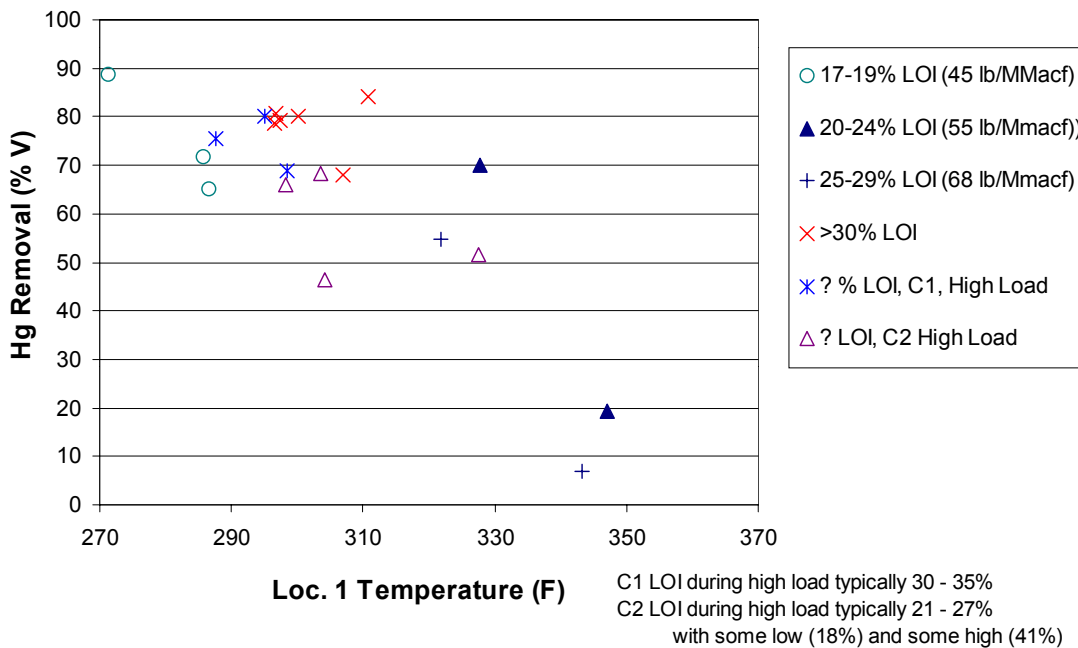


Figure 5. Hg Removal as a Function of Precipitator Inlet Temperature

Figure 6 shows the trend toward lower Hg emissions with higher LOI at an ESP inlet temperature of about 300 °F (plus or minus 10 °F). Fewer data were taken under constant temperature conditions, but the results suggest Hg capture greater than 50% when the LOI averages greater than 15%.

Hg Removal by Flyash LOI at Salem Harbor at ESP Inlet Temperatures of 290-310 F

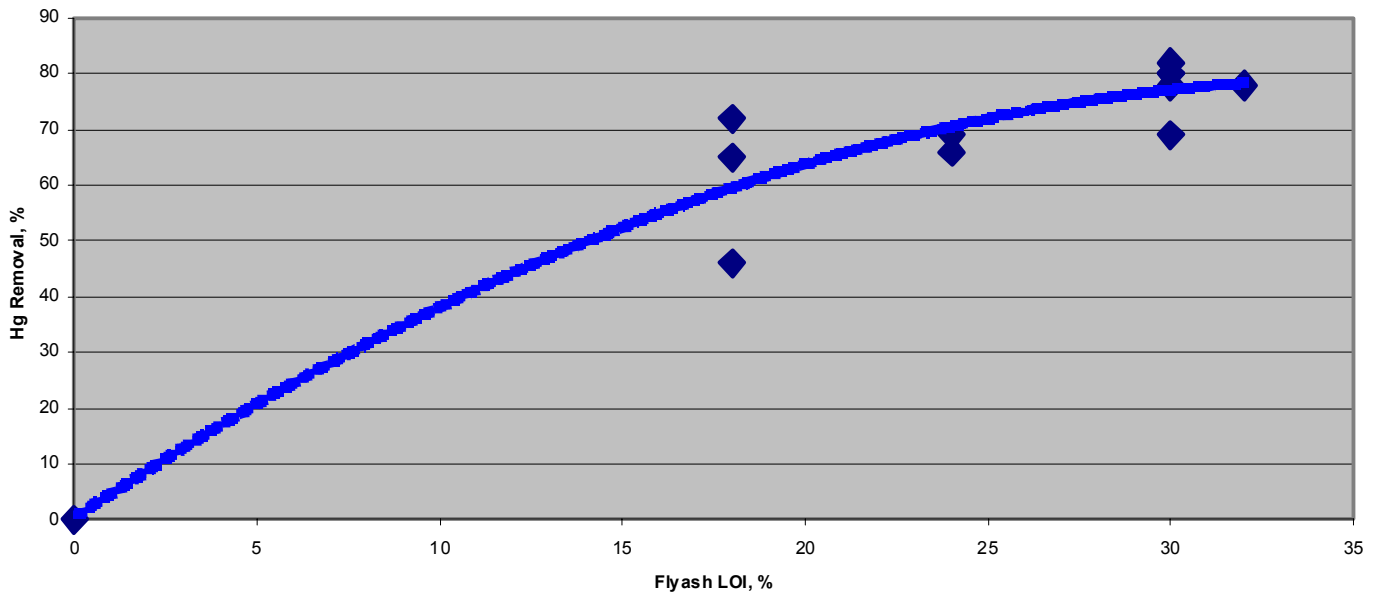


Figure 6. Hg Removal by Flyash LOI at 290-310 °F

Conceptual Hg Control System:

Mercury emissions from coal-fired boilers will be regulated sometime in the near future, with specific timetables specified already in some states (e.g. Massachusetts and New Hampshire). One way to take advantage of flyash LOI for reliable and cost-effective Hg emission compliance is illustrated on Figure 7. Requirements for LOI Hg capture include:

- **Greater than 15% LOI in fly ash**
 - Hg capture is linear function of LOI-Hg ratio.
 - Little benefit is gained from additional LOI above 20%
- **Flue gas temperature below 300 °F**
- **Sufficient time at that temperature before the ESP (at least 0.5 s)**

However, operating your combustion system to maintain 15 to 20 percent LOI has obvious practical constraints for most plants. First, flyash with this much carbon is difficult to sell to the cement industry. Even using the ash as a Btu-containing additive to cement kiln feed may be prohibited because the Hg would be re-released, thus requiring the cement kiln to install Hg controls. Therefore, the conceptual system in Figure 7 shows carbon (and Hg) separation from the flyash.

There are two commercial technologies now available to separate carbon from fly ash:

- Carbon burnout processes
- Tribo-electric separation processes

Carbon burnout has the disadvantage of releasing the Hg from the ash. However, recapture should not be as expensive since the Hg has been concentrated by two orders of magnitude.

Tribo-electric processes are effective in removing up to 90% of the Hg-containing carbon particles from the ash. Unfortunately, if the carbon content is above 15 percent, then several passes through the separator may be required. Therefore, tribo-electric carbon separation may be more expensive when applied for Hg control.

Another requirement for effective Hg capture on activated carbon is some chlorine in flue gas (need bituminous coal). Most sub bituminous coals contain very little chlorine, and what little Cl is released gets absorbed by the alkali in the fly ash. It is thought that the chlorine co-absorbs onto the carbon where it reacts with metallic Hg to hold it in the particle.

Combustion controls may not be capable LOI within 15-20% range for all coals and operating conditions. Therefore, a failsafe Hg control system may need an activated carbon injection system to be installed and held in stand-by. Capital costs for activated carbon storage and injection are relatively low (\$2-10/kW), but operating costs tend to be high (\$800-1000/ton). Significant operating costs can be avoided by using activated carbon only as needed.

Another necessary component of an Hg-control system is feedback from a continuous Hg Analyzer. This signal is needed to initiate the combustion controls. To date, no reliable continuous Hg analyzer is available for process control, but many companies (including ADA-ES) are striving to develop the necessary technology.

The Hg-removal system could also include a small fabric filter located downstream of the precipitator. This configuration is called TOXECON™ and was developed by EPRI. In this case, activated carbon would be injected upstream of the filter to improve carbon utilization (more Hg removed using less carbon) by about a factor of five. Additional benefits of the fabric filter would include:

- More effective removal of fine particulate (<2.5 micron)
- PAC segregation from the rest of the fly ash to prevent contamination. ADA has shown that even small amounts of activated carbon can cause ash to fail the foam test and thus preclude its use in the cement industry.

Quinny Concept for Hg Removal

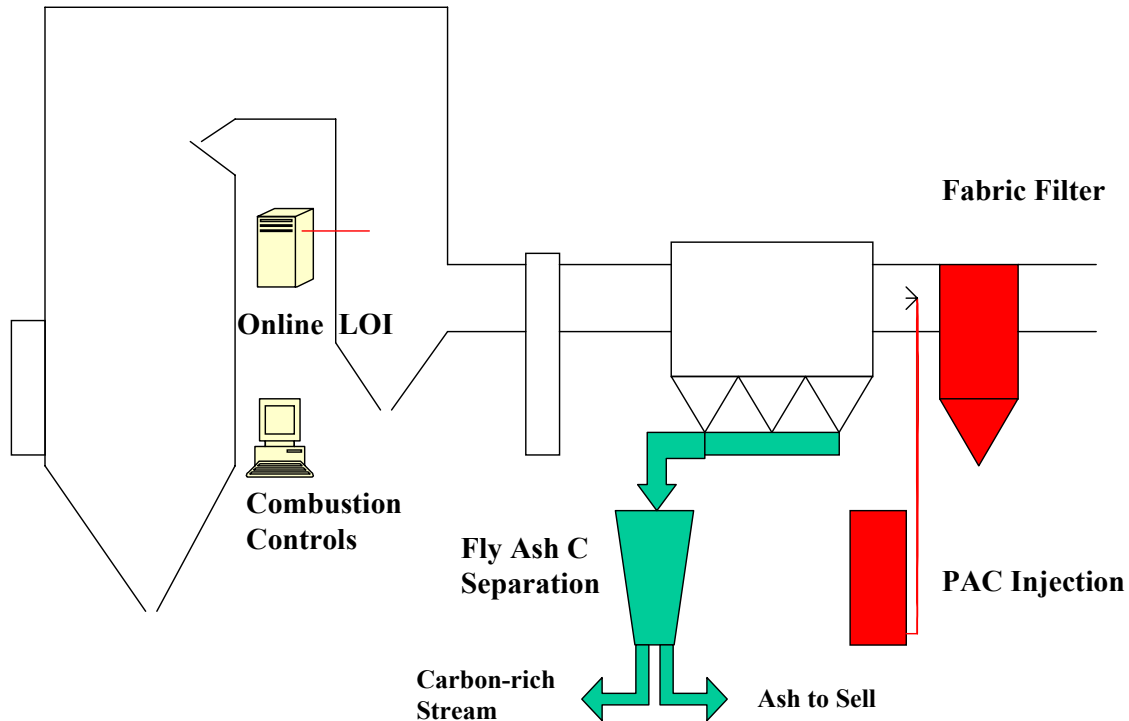


Figure 7. Conceptual Hg Control System for Coal-Fired Boilers

Conclusions:

Work at Salem Harbor suggests that over 50% of the Hg released during coal combustion can be captured by unburned carbon and removed in the electrostatic precipitator under some conditions. These conditions include:

- Bituminous coal
- Precipitator inlet temperature less than 300 °F
- Adequate time at this temperature for in-flight Hg sorption on the carbon particles
- Fly ash LOI greater than about 15 %. Lower LOI may remove more Hg when the flue gas temperature is below 270 °F.

The challenge to the savvy boiler operator will be to maintain these favorable conditions, with the help of instrumentation and combustion controls. Online LOI analysis may be the key to make Hg control feasible.

Reference:

1. T. Starns, J Bustard, R Afonso, S Sjostrom, R Chang, and S Renninger, “Results of Activated Carbon Injection Upstream of Electrostatic Precipitators for Mercury Control”, presented at the Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D.C., 19-22 May 2003.