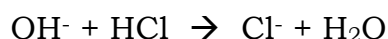


Mercury Control by Flue Gas Cooling and Conditioning

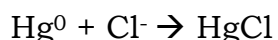
Prepared Exclusively for BES by Charles B Sedman

Mercury in combustion flue gas is present as elemental and oxidized mercury vapor and mercury sorbed on particles. Most fundamental studies support the concept that elemental mercury vapor is oxidized before being absorbed; therefore an oxidizing agent or site must be present to promote the capture of elemental mercury in an aqueous solution or sorption on a particle.

To understand how mercury behaves in flue gas, numerous studies of mercury sorbents and sorption have been conducted. The current models being used to predict mercury behavior are based upon these studies that show (1) homogeneous (gas-phase) mercury oxidation by free chlorine radicals in the flue gas followed by (2) heterogeneous (surface catalyzed) mercury oxidation and sorption on internal duct, sorbent, and fly ash surfaces. Homogeneous mercury oxidation (Figure 1) is straightforward and explained by the creation of chlorine radicals, Cl^\cdot , by the reaction of other radicals with HCl (formed from the combustion of various chlorine species in coal) by the so-called Deacon reaction:



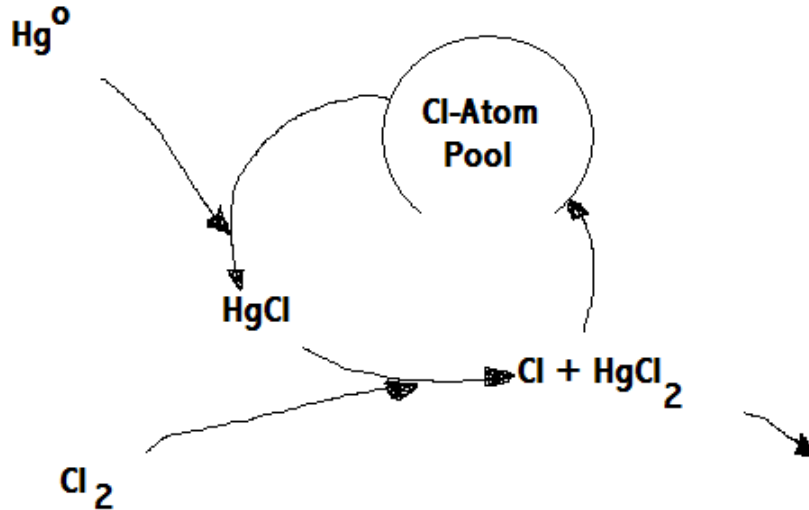
Once formed, the Cl^\cdot radical directly interacts with elemental mercury vapor, Hg^0 :



Then further reacts with free chlorine to form mercuric chloride, and regenerate the free chlorine radical:



This may occur in the furnace and probably at the surface of Selective Reduction catalysts, although mercury-SCR chemistry is still being studied. The extent of mercury vapor oxidation upstream of the air preheater is then mainly a function of the coal chlorine content, although other species such as sulfur oxides, water vapor, ammonia, and alkaline solids influence the actual amount of chlorine radicals available¹.



**Figure 1. Homogeneous Mercury Oxidation
(Gas-Phase)**

Small-scale Studies of Heterogeneous Mercury Behavior on Carbon Surfaces

Downstream of the airheater, physical sorption processes dominate. These phenomena are very complex. To date the best collected works are summarized in a recent paper by the University of North Dakota (UNDEEC), which explain the role of flue gas acids and carbon sorbents as follows² (Figure 2):

- (1) Oxidation of Hg^0 occurs by transfer of electrons to the carbon surface, yielding Hg^{++} or Hg(II) ions;
- (2) Binding of Hg(II) takes place at Lewis Base sites on the carbon, not necessarily on other alkaline material present;
- (3) The Lewis Base sites are eventually occupied by SO_2 and Hg(II) salts are displaced and volatilized as HgCl_2 or $\text{Hg(NO}_3)_2$.

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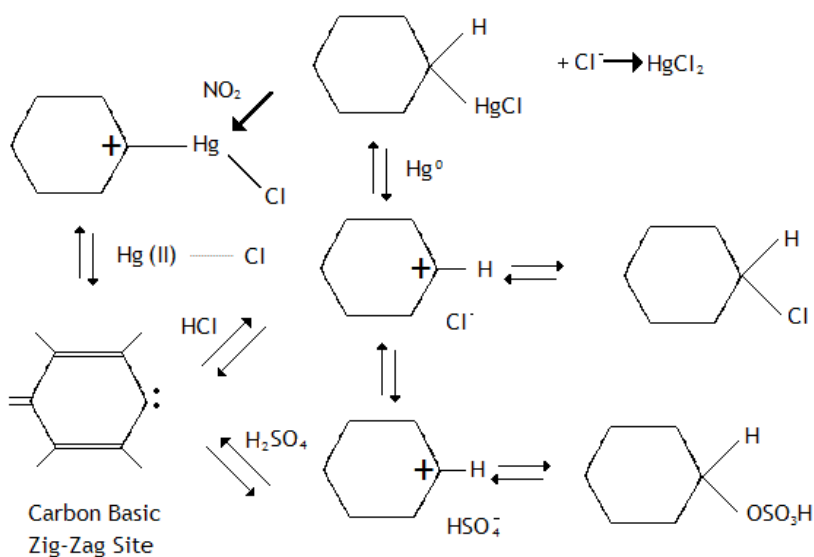


Figure 2. Mercury Oxidation on Carbon Surfaces

Unfortunately, the UNDEEC work was conducted in the absence of flue gas sulfuric acid, which may alter the results somewhat, since they additionally observe that, “HCl or other protonic acids promote the oxidation step by generating the positive carbenium ion oxidation sites, but the reaction site eventually becomes cluttered with sulfuric acid molecules.”

Complementary studies of mercury-solids behavior on carbon surfaces by EPA reinforce the observations of the UNDEEC studies. One study³ of activated carbon (AC)-mercury interactions showed conclusively that acid treatment of AC (in this case HNO_3) promoted the following:

- significant increase in mercury uptake
- decrease in pore volume and surface area
- increase in total oxygen concentration
- increase in carbon-oxygen surface groups

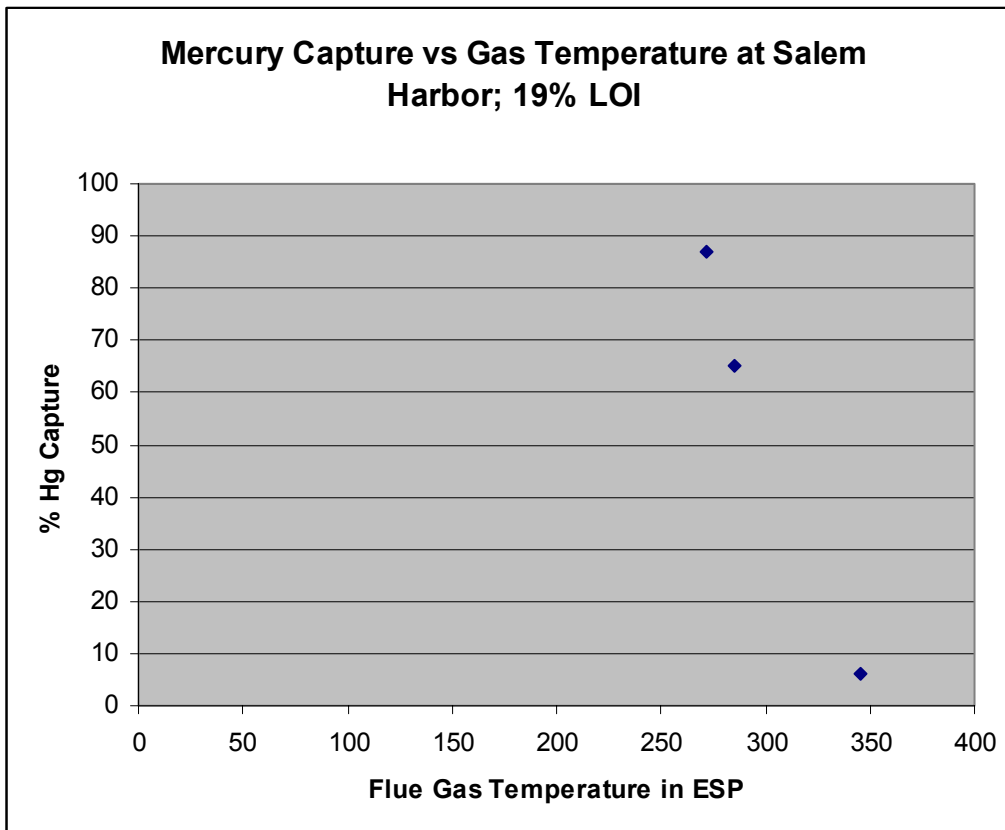
The study concludes that “the mechanism of Hg^0 absorption involves an electron transfer process and the carbon surface may act as an electrode for Hg^0 oxidation.”

Other indications of the action of acid species with active carbon species is evidenced in a number of patented processes for improving the mercury capture of

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AC, beginning with sulfuric acid treatment of AC, U.S. Patent 3,876,393, April 8, 1975.⁴

Observed mercury behavior at commercial utility boilers suggest that similar mercury oxidation and capture phenomena may occur on the unburned carbon of fly ash, called “intrinsic capture”. One recent study of mercury behavior cites the effect of flue gas temperature and unburned carbon as very important, as illustrated at the Salem Harbor plant of PG&E Generating⁵. At the lowest fly ash LOI (17-19%), mercury capture ranged from below 10% at an ESP temperature of 345°F to nearly 90% at 270°F. Both EPRI and EPA are beginning bench and pilot studies of fly ash LOI, flue gas acids and temperature to better develop a predictive model. It appears, therefore, that the same phenomena observed by UNDEEC in their bench studies also occur on the LOI of fly ash.



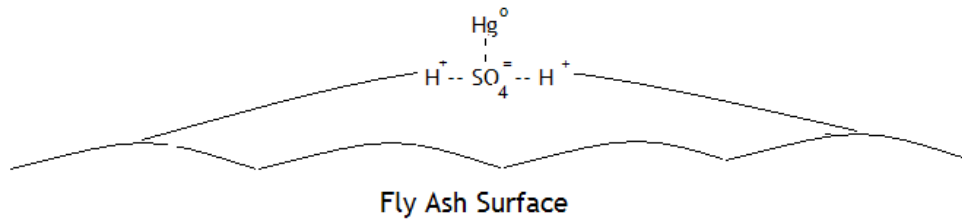
Mercury Behavior on Non-Carbon Surfaces

But the phenomena of mercury vapor oxidation and capture is not limited to carbon surfaces. Other EPA studies of non-carbon mercury sorption are significant. Using calcium-based sorbents - $\text{Ca}(\text{OH})_2$ and CaSiO_3 - in an flue gas containing only O_2 ,

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N_2 , CO , CO_2 , H_2O and Hg^0 with no fly ash or chlorine present, significant Hg^0 uptake was observed when the sorbent samples were hydrated with oxidants then exposed to the flue gas in a fixed bed for two hours at temperatures from 80-100°C⁶. When SO_2 was removed from the flue gas, no Hg^0 uptake was observed. This suggests that oxidants do not directly oxidize Hg^0 ; rather another intermediate species must be present to oxidize mercury. In this case, the only possible intermediate species would be SO_3 , and for this temperature range, SO_3 would all be combined with flue gas moisture as H_2SO_4 (Figure 3). The higher pore area silicate sorbents showed proportionally higher Hg^0 uptake than the hydrated lime sorbents.

Figure 3. Hg^0 oxidation by Condensed H_2SO_4



Another study looked at capacities of alkaline sorbents for Hg^0 at 60°C in the presence of HCl and ranked them as follows⁷:

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Table 1
Hg⁰ Uptake by the HCl-exposed Ca-based Sorbents

Sorbent Type	Cl Uptake, µg/g	Hg ⁰ Uptake, µg/g
Ca(OH) ₂	60000	0.108
CaO	16000	0.828±0.046
CaCO ₃	2400	0.587±0.065
CaSO ₄ ·2H ₂ O	3600±200	2.27±0.056

This study concludes that HCl physical adsorption, through hydrogen bond formation, in Ca-based compounds with crystalline water (CaSO₄·2H₂O and CaSO₄·½H₂O) was shown to be responsible for promoting Hg⁰ uptake. It was hypothesized that a pair of physically adsorbed HCl molecules can attract and adsorb an Hg⁰ molecule possibly through attractive van der Waals forces to form an HgCl₂-like molecule. The amount of Hg⁰ uptake was correlated to the amount of crystalline water for Ca-based sorbents. Again no H₂SO₄ was present in these experiments.

Once mercury is in its oxidized form, capture is then a function of the number of “traps” and the residence time or exposure time of oxidized mercury in these traps. Another study by EPA looked at the bonding of mercuric chloride with alkaline materials⁸ and concludes that weak Van der Waals forces are primarily responsible for the initial capture of ionic mercury via uni- and bi-dentate bonds (Figure 4). The results of this study – fixed-bed sorption at 80, 100 and 140°C are shown in Table 2, below:

Table2. Alkaline Sorbent Properties and HgCl₂ Capacities.

Sorbent	pH	BET Surface Area (m ² /g)	Avg. pore diameter (µm) (□)	D ₅₀	Porosity	Surface Basicity (mmole/m ²)	HgCl ₂ Capacity (mg HgCl ₂ /g)			
							Q ₆₀	Q ₁₀₀	Q ₁₄₀	
Ca(OH) ₂	11.95	14.510	248	6.25	0.156	0.033	0.4469	0.2020	0.0800	
CaO	11.95	4.525	5840	7.01	0.065	0.017	0.4471	0.0538	0.0153	
CaCO ₃	9.64	0.9042	4130	23.69	0.006	n/a	0.4594	0.0509	0.0111	
CaSO ₄	7.4	6.605	198	29.09	0.069	n/a	0.3595	0.1152	0.0039	
NaHCO ₃	8.35	14.305	500	53.9	0.161	n/a	0.2416	0.1467	0.0358	
Na ₂ CO ₃	10.98	0.9582	221	300	0.006	0.032	0.2814	0.0551	0.0188	
NaOH	12.01	0.2546	252	300	0.001	2.530	0.0000	0.0978	0.0085	
Na ₂ SO ₄	6.65	0.2031	74.4	88.94	0.001	n/a	0.1847	0.0424	0.0090	
K ₂ CO ₃	10.98	0.5718	111	300	0.003	0.124	0.4102	0.0409	0.0090	
K ₂ SO ₄	7.37	0.4448	110	30.64	0.002	n/a	0.2047	0.0253	0.0028	
Mg(OH) ₂		10.21	10.91	315	9.61	0.152	0.002	0.2900	0.0370	0.0024

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As shown above, most alkaline sorbents rapidly lose their mercury sorption capacities with increasing temperature, indicating the physical nature of the bond. In spite of the weakness of these physical bonds, thermal desorption experiments consistently show that alkaline sorbents typically retain more mercury than activated carbon. This leads to the conclusion that mercury capture with weak physical bonds occurs in small pores, and the closure of pores by reactions between flue gas acids and alkaline sorbents at lower flue gas temperatures effectively entomb the sorbed mercury species in the pores.

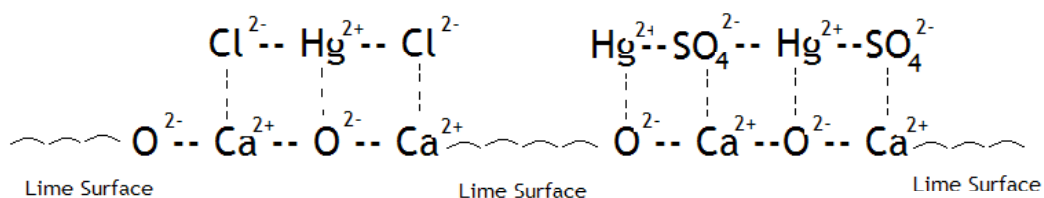


Figure 4. Bi-Dendate Bonding of Oxidized Mercury Vapor on Calcium Oxide

Interpretation of Mercury Studies and Implications

Mercury vapor control is essentially that of providing acid species, reactive sites, and proper temperatures and reaction times. If an existing system is to be modified for mercury capture, then the choices are any or a combination of the following:

- (1) modify fly ash carbon content by combustion modifications or add carbon sorbent;
- (2) lower flue gas temperature as much as practicable entering the PM collector;
- (3) add flue gas or solids residence time
- (4) add flue gas acids

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(5) add more non-carbon surface for reactions

and most importantly,

(6) only add alkalinity to the system for acid species capture [including Hg(II)] after adequate mercury oxidation has been ensured upstream

The practical limitations of the above are a separate discussion, especially if concurrent control of other pollutants are factored in. It should be noted here that alkaline fly ash, as found in lignite and subbituminous coal applications present a special case, since:

- (1) inherent fly ash LOI is very low;
- (2) acid species (HCl, SO₃) are inherently low and absorbed rapidly by alkaline ash as flue gas temperature is lowered;
- (3) Free chlorine radicals in the combustor are sequestered by alkaline ash.

Because of these system limitations, it is practically imperative that lignite and subbituminous coal mercury control begin with installation of a fixed-bed (baghouse) or fluidized bed reactor for long solids residence times and good gas-solids contact..

Recommended System For Most Non-scrubbed Applications

- 1. The DAP (evaporational cooling only) can satisfy the needs for simultaneous gas cooling, increased surface by internal recirculation of larger solids, and increased gas-solids contact.**
- 2. Where acid gases are insufficient to promote nearly complete mercury oxidation, additional acid may be added by SO₃ injection or H₂SO₄ addition with the cooling water.**
- 3. An alkaline species should be added between the initial DAP reactor and the PM collector to both protect the PM collector and ductwork from acid attack and promote additional capture of mercury species; lime is preferred since both lime and calcium sulfate hydrates are shown to sorb Hg(II) effectively.**
- 4. Additional carbon surface can be added by fly ash or activated carbon injection, but this should take place well upstream of the DAP reactor to allow the carbon to form the carbene-acid species necessary for mercury oxidation and capture.**
- 5. An alternative to additional carbon would be to add an oxidant with the lime addition downstream of the DAP evaporational cooler/reactor.**

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- 6. If additional acid gas (HCl, SO₂) control is desired, then the RAP should be staged such that evaporational cooling and condensing of H₂SO₄ takes place before bulk acid gases are reacted with lime or other alkaline sorbent,**
- 7. For alkaline ash applications, more acid may be necessary to create a surface calcium sulfate layer on the ash, capable of supporting a free sulfuric acid condensate necessary for oxidizing mercury. Alternately an oxidant may be added with substantially less cooling water in the DAP to promote NO₂ formation and subsequent mercury oxidation well upstream of any bulk acid gas removal.**

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