

Mercury Chemistry in Flue Gas Cleanup Systems

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Argonne's Research Has Addressed Important Mercury Control Options

- **Characterization and comparison of activated carbons and other dry sorbents designed for duct injection**
- **Investigation of low-cost dry sorbents based on chemical treatment of inert substrates**
- **Evaluation of oxidants for changing mercury speciation in flue gas**
- **Development of a process to enhance mercury and NO_x removal using oxidants**
- **Analysis of available literature data on mercury oxidation in a critical review; application of the results to specific mercury control issues**

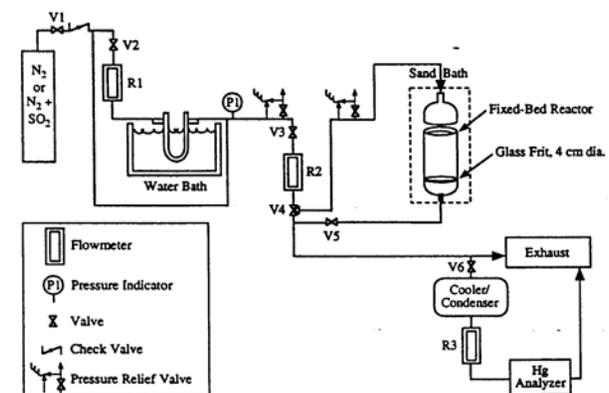
Dry Sorbent Testing and Development Has Used a Fixed-Bed Reactor System

- Treatment of powdered pumice with halogen compounds or sulfur gave promising results
- One **sulfur-treated sorbent performed essentially the same as a commercial sulfur-impregnated activated carbon but with lower projected cost**



- **References:**

- Livengood, C.D., et al., *Enhancement of Mercury Control in Flue-Gas Cleanup Systems*, U.S. DOE/PETC First Joint Power & Fuel Systems Contractors Conference, Pittsburgh (July 9-11, 1996)
- Huang, H.S., et al., *Development of Dry Control Technology for Emissions of Mercury in Flue Gas*, Hazardous Waste & Hazardous Materials, 13 (1), 107-119 (1996)



Wet Scrubbing Tests Investigated Oxidants in Both the Gas and Liquid

- Halogen species in the scrubber liquor oxidized Hg^0 , but also reacted strongly with other gas components
- Chloric acid in the gas phase gave excellent removal of Hg^0 and enhanced removal of NO
- References/Patents:
 - Livengood, C.D., and M.H. Mendelsohn, *A Process for Combined Control of Mercury and Nitric Oxide*, 94th Annual Conference & Exhibition of the Air & Waste Management Association, Orlando, Florida, June 24-28, 2001
 - Mendelsohn, et al., *Method for the Removal of Elemental Mercury from a Gas Stream*, U.S. Patent 5,900,042 (1999)
 - Mendelsohn, M.H., and C. D. Livengood, *Method for Combined Removal of Mercury and Nitrogen Oxides from Off-Gas Streams*, U.S. Patent application allowed.



Wet Scrubber



Simulated
Flue-Gas
Duct

The Chemistry of Hg is Clearly a Key Element for Control Processes

- Difficulty in understanding/predicting emissions indicated that a better understanding of Hg chemistry was needed.
- Argonne carried out a **critical review of published information** to establish the state of existing knowledge and identify research needs.
- **References:**
 - Livengood, C.D., et al., *Mercury Chemistry in Flue Gas, A Critical Review*, 97th Annual Conference & Exhibition of the Air & Waste Management Association, Indianapolis, Indiana (June 22-25, 2004)
 - Topical Report in Preparation



The Critical Review:

- Focused on **chemical mechanisms for the homogeneous gas-phase chemistry of Hg^0 with Cl_2 and HCl .**
- Searched the technical literature back to **1907**, assembling the most relevant documents publicly available, and critically reviewing over 300 pages of material.
- Found that:
 - The earliest relevant paper was published in **1949**.
 - Detailed mechanistic models began appearing in **2000**.
 - Later work (up to **March 2003**) produced new kinetic data and model revisions that incorporated more chemical species and the effects of particulate matter.



Early Papers Gave Much Different Views of Reaction Kinetics

- ***Surface Catalyzed Reaction of Hg + Cl₂*, A. K. Medhekar, M. Rokni, D. W. Trainor, and J. H. Jacob, Chem. Phys. Lett., 65 (3), 600-604 (1979): found a fast reaction for Hg⁰ with Cl₂, but attributed this to a surface-catalyzed reaction**
- ***Detection of Mercury in Air in the Presence of Chlorine and Water Vapor*, R. Menke and G. Wallis, Am. Ind. Hyg. Assoc. J., 41 (2), 120-124 (1980): found a slow reaction for Hg⁰ with Cl₂; rate constant calculated from the data in this paper is cited (directly or indirectly) in later atmospheric chemistry research papers**



A Later Paper Confirmed a Slow Gas-Phase Reaction

- ***Reactions Between Mercury Vapor and Chlorine Gas at Occupational Exposure Levels, A. Skare and R. Johansson, Chemosphere, 24 (11), 1633-1644 (1992):***
 - **First independent laboratory data that agreed with results of Menke and Wallis (1980), finding a slow homogeneous gas-phase reaction of Hg^0 with Cl_2 at room temperature**
 - **Results showed that 40% of gaseous Hg^0 disappeared after standing with gaseous Cl_2 for 24 hr in a Tedlar bag**
 - **This corresponds to a rate at least 10^5 times slower than that found for the surface catalyzed reaction**



Between 1998 and 2003, a Number of Hg^0 Oxidation Mechanisms were Proposed:

- The 8-step Hg/Cl oxidation sub-mechanism below first appeared in **2000** and has been widely accepted and used in later work as part of an overall homogeneous gas-phase mechanism:

- 1. $\text{Hg}^0 + \text{Cl} + \text{M} \rightleftharpoons \text{HgCl} + \text{M}$
- 2. $\text{Hg}^0 + \text{Cl}_2 \rightleftharpoons \text{HgCl} + \text{Cl}$
- 3. $\text{Hg}^0 + \text{HCl} \rightleftharpoons \text{HgCl} + \text{H}$
- 4. $\text{Hg}^0 + \text{HOCl} \rightleftharpoons \text{HgCl} + \text{OH}$
- 5. $\text{HgCl} + \text{Cl}_2 \rightleftharpoons \text{HgCl}_2 + \text{Cl}$
- 6. $\text{HgCl} + \text{Cl} + \text{M} \rightleftharpoons \text{HgCl}_2 + \text{M}$
- 7. $\text{HgCl} + \text{HCl} \rightleftharpoons \text{HgCl}_2 + \text{H}$
- 8. $\text{HgCl} + \text{HOCl} \rightleftharpoons \text{HgCl}_2 + \text{OH}$



Gas-Solid Interactions were Later Added to the Mechanism



- ***A Mechanism for Mercury Oxidation in Coal-Derived Exhausts*, S. Niksa, N. Fujiwara, Y. Fujita, K. Tomura, H. Moritomi, T. Tuji, and S. Takasu, J. Air & Waste Manage. Assoc., 52, 894-901 (2002):**
 - **First model to include gas-solid interactions along with 102 homogeneous gas-phase reactions**
 - **Proposed a simple 3 step mechanism for gas-solid interactions:**
 - $\text{StSA (s)} + \text{HCl} \text{ ----> StCl (s)} + \text{H}$**
 - $\text{StCl (s)} + \text{Cl} \text{ ----> Cl}_2 + \text{StSA (s)}$**
 - $\text{StCl(s)} + \text{Hg}^0 \text{ ----> StSA (s)} + \text{HgCl}$**

where StSA(s) denotes an unoccupied carbon site and StCl(s) denotes a chlorinated site

Issues and Recommendations

- **Homogeneous Reaction Mechanisms:**
 - Both Cl_2 and Cl appear to be vital species in a Hg^0 oxidation mechanism. What effects do other flue-gas species have on the Hg^0 oxidation mechanism?
- **Heterogeneous Reaction Mechanisms:**
 - What influences do coal type, combustion conditions, and flue-gas composition have on particulate active sites?
- **Reaction Kinetics:**
 - Improved values of the rate constants for reactions of Hg^0 with Cl_2 and Cl are available and should be used in future modeling studies.
 - The reaction of Hg^0 with Cl may be the most important (i.e., rate determining) step of the 8-step model because reactions involving HgCl are assumed to be fast. The rate constant for the reaction of either Cl_2 or Cl with HgCl should be checked experimentally.



A Further Review of the Literature Was Conducted for Wet Scrubbing of Hg

- The focus was on the phenomenon of **“re-emission” of Hg^0 from wet FGD scrubbers**
- Wet scrubbers readily absorb oxidized Hg species such as HgCl_2 , but absorb very little of the elemental form, Hg^0
- In some cases, measurements have found more Hg^0 leaving the scrubber than was measured at the inlet
- A mechanism that can reduce oxidized mercury to the elemental form is implied
- Published information on this topic is relatively sparse



Proposed Mechanisms Involve the Interaction of Mercury and Sulfur Species

- **Several papers suggest the reaction of mercuric chloride with sulfur (IV) species such as sulfite/bisulfite, followed by decomposition of the Hg•S(IV) complexes yielding Hg⁰ (Chang and Ghorishi, 2003; Blythe, et al., 2004)**
- **Mercuric ions can form either 1:1 or 1:2 coordination compounds with sulfite ions, but Hg²⁺ reduction appears associated with the 1:1 species (HgSO₃)**
- **Higher sulfite/bisulfite ratios favor re-emission**
- **Higher temperatures (kinetics) and higher pH (sulfite/bisulfite ratio) favor re-emission**



Proposed Mechanisms (cont.)

- **Solids in the scrubber slurry retard re-emission to different degrees depending on the nature of the solids (Akiho, et al., 2003)**
- **One study (van Loon, et al., 2001) postulates the formation of an $\text{Hg}^0 \cdot \text{SO}_2$ complex from the decomposition of HgSO_3 ; the complex could retard re-emission due to its high solubility relative to Hg^0**

Ongoing Work is Reviewing Information on Hg Oxidation by Fly Ash

- Some field data have indicated significant mercury **oxidation across a baghouse** collecting ash from PRB coal – is this a characteristic of PRB?
- Ash particles can be sites for oxidation, but any differentiation with coal rank between bituminous and subbituminous is inconclusive (Dunham, et al., 2003)
- The metal-catalyzed reaction of HCl to form Cl_2 via a “Deacon-type” reaction may be significant
- Fe_2O_3 and CuO have been cited as important for oxidation of Hg^0 (Ghorishi, et al., 1999)
- Published trace-element data do not show PRB coals to be enriched in Fe or Cu relative to bituminous

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