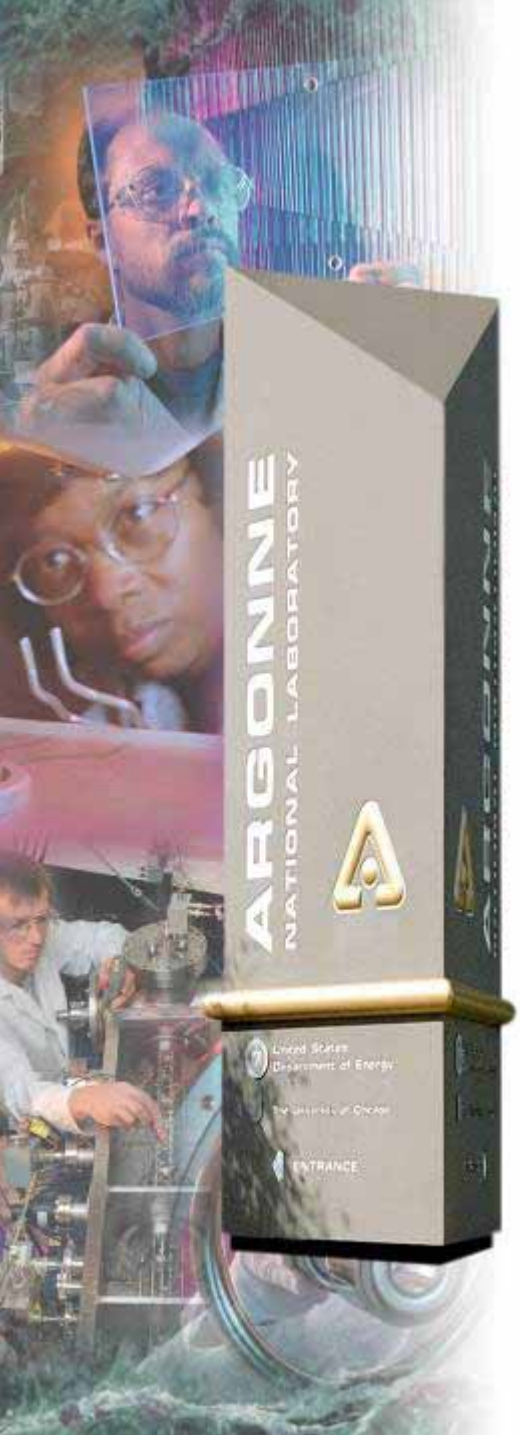

The Chemistry of Mercury Oxidation

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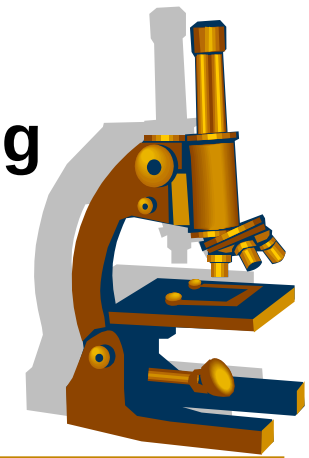
The Chemistry of Hg in Flue Gas is a Key Element in Control Processes

- **Difficulty in understanding/predicting emissions indicated that a better understanding of Hg chemistry was needed.**
- **A critical review of published information established the state of existing knowledge and identified research needs.**
- **Advanced analytical techniques are being investigated for their application to challenging research problems.**



The Critical Review Involved:

- **A survey of mercury experts to help focus the review on the most important issues.**
- **Identification of chemical mechanisms for the homogeneous gas-phase chemistry of Hg^0 with Cl_2 and HCl as the initial focus.**
- **A search of the literature back to 1907, assembling the most relevant documents publicly available, and critically reviewing over 300 pages of material.**
- **Development of a topical report (in preparation) and meeting presentations (A&WMA, 2004).**

The Most Significant Literature is Relatively Recent

- **The earliest relevant paper was published in 1949.**
- **Interest in lasers produced several papers in the 70s and 80s on mercury in excited states.**
- **Two significant early papers were found in ’79 and ’80.**
- **Renewed interest in the late 80s and early 90s produced several more important papers.**
- **Detailed mechanistic models began appearing in 2000.**
- **Recent work (up to March 2003) has produced new kinetic data and model revisions that incorporate more chemical species and effects of particulate matter.**

Early Papers Gave Much Different Views of Reaction Kinetics

- ***Surface Catalyzed Reaction of Hg + Cl_2*, 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 Hg^0 with Cl_2, 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 Hg^0 with Cl_2; 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. $Hg^0 + Cl + M$ <-----> $HgCl + M$**
  - **2. $Hg^0 + Cl_2$ <-----> $HgCl + Cl$**
  - **3. $Hg^0 + HCl$ <-----> $HgCl + H$**
  - **4. $Hg^0 + HOCl$ <-----> $HgCl + OH$**
  - **5. $HgCl + Cl_2$ <-----> $HgCl_2 + Cl$**
  - **6. $HgCl + Cl + M$ <-----> $HgCl_2 + M$**
  - **7. $HgCl + HCl$ <-----> $HgCl_2 + H$**
  - **8. $HgCl + HOCl$ <-----> $HgCl_2 + OH$**

Gas-Solid Interactions were Recently 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:

  a. StSA (s) + HCl -----> StCl (s) + H

  b. StCl (s) + Cl -----> Cl_2 + StSA (s)

  c. StCl(s) + Hg^0 -----> StSA (s) + 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. Can the concentrations of either of these be measured at various locations in a real-world flue-gas stream?**
  - **Since HCl can react with O_2 to form Cl_2 via a Deacon-type process, can the extent of this pathway either be estimated or measured?**
  - **What effects do other flue-gas species have on a Hg^0 oxidation mechanism?**
- **Heterogeneous Reaction Mechanisms:**
  - **Because of the potential importance of gas/solid reactions in Hg^0 oxidation, an assessment should be made of plausible gas/solid mechanisms.**
  - **What influence does coal type, combustion conditions, and flue-gas composition have on particulate active sites?**

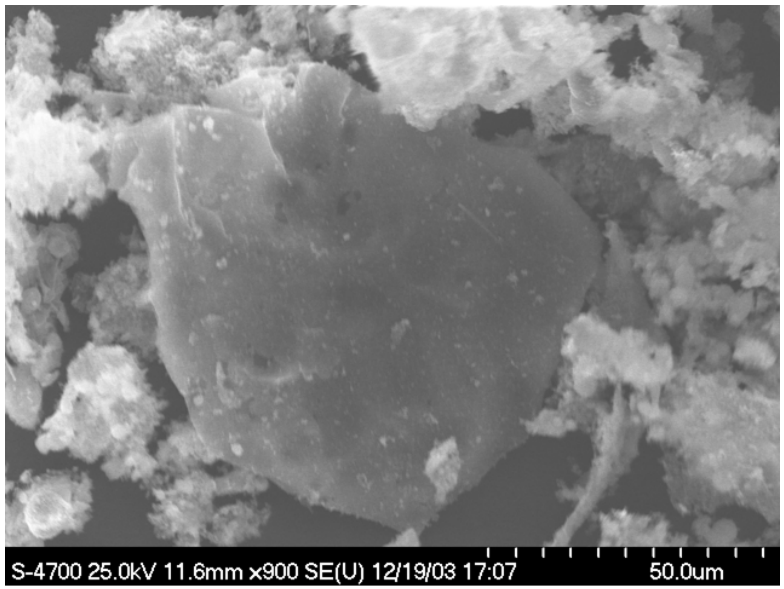
Issues and Recommendations

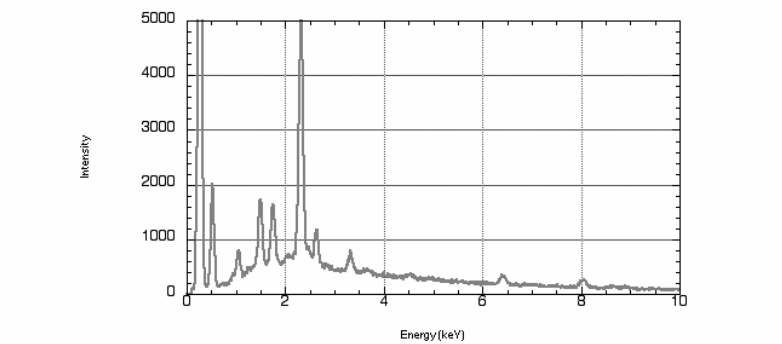
- **Reaction Kinetics:**
  - **Recent, improved values of the rate constants for reactions of Hg^0 with Cl_2 and Cl are available and should be used in future modeling studies.**
  - **Do these new values have any substantial effects on the results of previous model calculations?**
  - **Several workers consider the reaction of Hg^0 with atomic-Cl to be the most important (i.e., rate determining) step of the 8-step model because reactions involving HgCl are assumed to be fast. However, the rate constant for the reaction of HgCl with either Cl_2 or Cl should be checked in the lab.**

Techniques to Study Interactions of Hg with Solids Are Being Evaluated

- **Initial objective is to identify physical/chemical associations for Hg on particles**
- **Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray (EDX) analysis can image individual ash particles and chemically analyze small regions.**
  - **Detection limit of about 1000 ppm for most elements**
  - **Only elements in near-surface region detected**
  - **Areas of high local concentration are needed to find elements with average levels below 1000 ppm**
  - **Identification of "promising" regions or features for Hg is the current challenge**

Initial Tests Did Not Find Hg on Fly Ash, but Did Find Cu Present at 1.9 ppm (avg.)





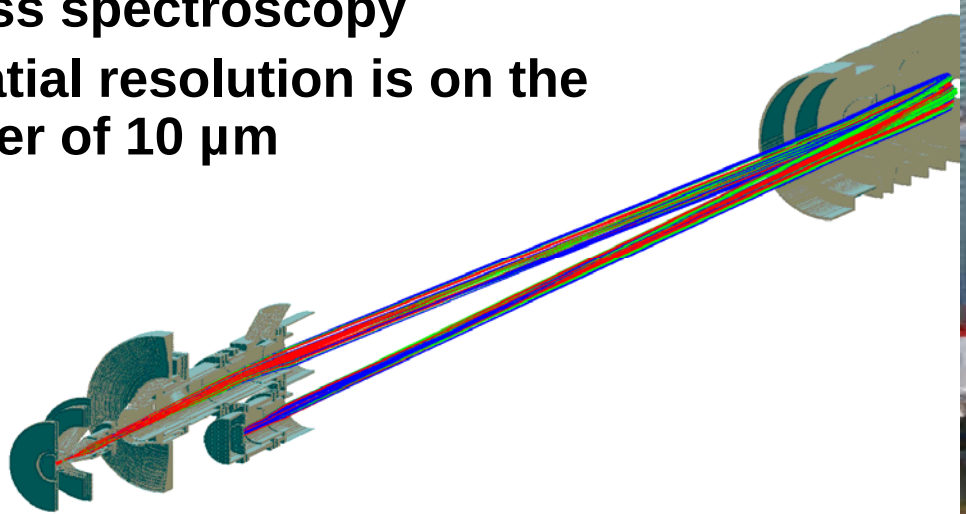
Element	Energy (keV)
C	0.28
O	0.53
Na	1.04
Al	1.49
Si	1.74
S	2.31
Cl	2.62
K	3.31
Fe	6.40
Cu	8.04

Another Ash Particle from the Same Boiler Showed No Cu and Negligible S

Element	Energy (keV)
C	0.28
O	0.53
Mg	1.25
Al	1.49
Si	1.74
K	3.31
Fe	6.40

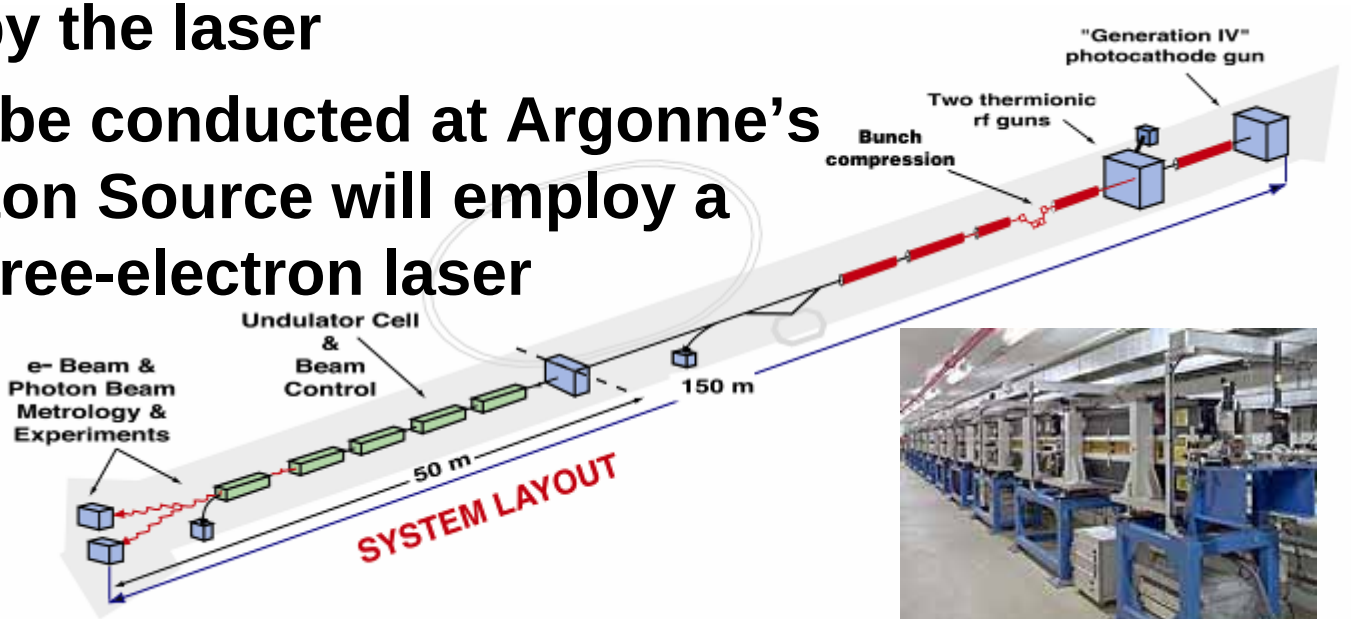
A New Technique Offers Sensitivities of 100 ppt or better

- **Laser Post Ionized Secondary Neutral Mass Spectrometry**
  - A beam of energetic Ar ions removes atoms from the surface being studied
  - Laser light ionizes the atoms, which are analyzed using time-of-flight mass spectroscopy
  - Spatial resolution is on the order of 10 µm



Initial Tests Indicated that a More Energetic Laser is Required

- **A sample of Sn-Hg alloy containing 650 ppm Hg was tested**
- **Sn atoms were readily detected using a 7.90 eV laser, but Hg was not found**
- **The unusually high ionization energy of Hg may not have been reached by the laser**
- **Future work to be conducted at Argonne's Advanced Photon Source will employ a higher energy free-electron laser**



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