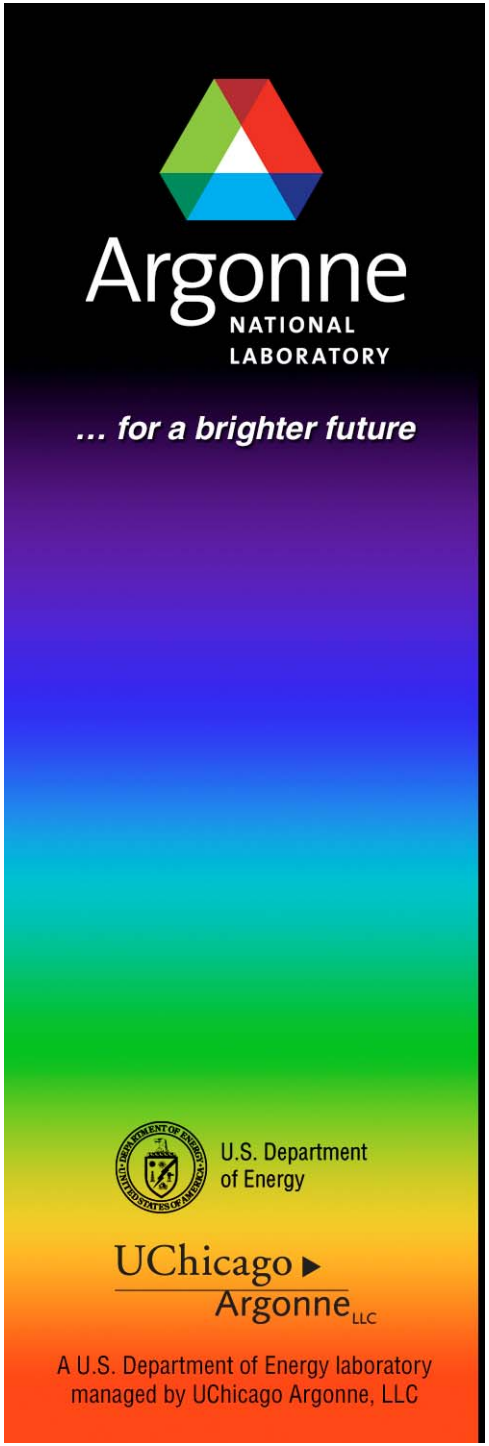


MERCURY CHEMISTRY IN FLUE-GAS TREATMENT SYSTEMS: ANALYSIS AND APPLICATIONS

C. David Livengood

David K. Schmalzer (presenter)

Argonne National Laboratory

Presented at

Mercury Control Technology Conference

December 11-13, 2006

Pittsburgh, Pennsylvania

Argonne's Research Has Addressed Important Mercury Control Options

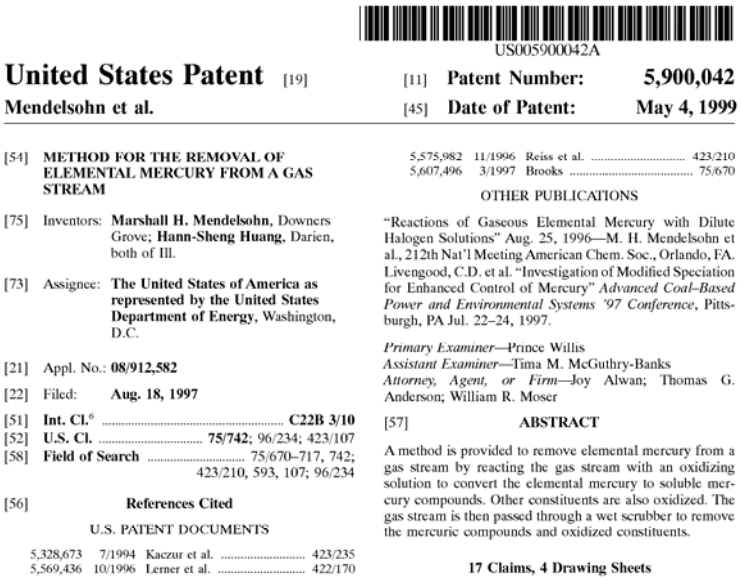
- **Characterization and comparison of activated carbons and other dry sorbents designed for duct injection**
- **Investigation of low-cost dry sorbents based on chemical treatment of inert substrates**
- **Evaluation of oxidants for changing mercury speciation in flue gas**
- **Development of a cost-effective 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**

Initial Research on Wet Scrubbing for Control of Mercury Demonstrated:

- **Limited potential for direct scrubbing of Hg^0 even with enhanced scrubbing measures**
- **Ability of several halogen species and compounds to affect mercury speciation by converting Hg^0 to a soluble form**
- **Possible synergism between Hg^0 and NO removals**
- **Negative effects of SO_2 on Hg^0 conversion**

Results of the Initial Research Led to a Patent on the Mercury Removal Method

- **METHOD FOR THE REMOVAL OF ELEMENTAL MERCURY FROM A GAS STREAM**
- **U.S. Patent 5,900,042; May 4, 1999**
- **Marshal H. Mendelsohn and Hann S. Huang**
- **ABSTRACT:**
  - **A method is provided to remove elemental mercury from a gas stream by reacting the gas stream with an oxidizing solution to convert the elemental mercury to soluble mercury compounds. Other constituents are also oxidized. The gas stream is then passed through a wet scrubber to remove the mercuric compounds and oxidized constituents.**



US005900042A

United States Patent [19]
Mendelsohn et al.

[11] **Patent Number: 5,900,042**
[45] **Date of Patent: May 4, 1999**

[54] **METHOD FOR THE REMOVAL OF ELEMENTAL MERCURY FROM A GAS STREAM**

[75] Inventors: **Marshall H. Mendelsohn**, Downers Grove; **Hann-Sheng Huang**, Darien, both of Ill.

[73] Assignee: **The United States of America as represented by the United States Department of Energy**, Washington, D.C.

[21] Appl. No.: **08/912,582**

[22] Filed: **Aug. 18, 1997**

[51] **Int. Cl.**[6] **C22B 3/10**
[52] **U.S. Cl.** **75/742**; 96/234; 423/107
[58] **Field of Search** 75/670–717, 742; 423/210, 593, 107; 96/234

[56] **References Cited**

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"Reactions of Gaseous Elemental Mercury with Dilute Halogen Solutions" Aug. 25, 1996—M. H. Mendelsohn et al., 212th Nat'l Meeting American Chem. Soc., Orlando, FA. Livengood, C.D. et al. "Investigation of Modified Speciation for Enhanced Control of Mercury" *Advanced Coal–Based Power and Environmental Systems '97 Conference*, Pittsburgh, PA Jul. 22–24, 1997.

Primary Examiner—Prince Willis
Assistant Examiner—Tima M. McGuthry-Banks
Attorney, Agent, or Firm—Joy Alwan; Thomas G. Anderson; William R. Moser

[57] **ABSTRACT**

A method is provided to remove elemental mercury from a gas stream by reacting the gas stream with an oxidizing solution to convert the elemental mercury to soluble mercury compounds. Other constituents are also oxidized. The gas stream is then passed through a wet scrubber to remove the mercuric compounds and oxidized constituents.

17 Claims, 4 Drawing Sheets

Summary of Hg^0 removal results for large–bubble tests with chlorine solutions.

Feed–Gas Composition	Chlorine Concentration (ppm) 2.5	250	1,000	2,500	5,000
	Hg^0 Removal (%)				
$O_2+N_2+Hg^0$	11.6	14,4,13.3	--	9.3	14.3
$O_2+N_2+NO+CO_2+Hg^0$	19.0	20.6 [a]	35.4,28.1	37	44.5
$O_2+N_2+NO+CO_2+SO_2+Hg^0$	0.5	13.8	35.1,34	35.4,41	52.2

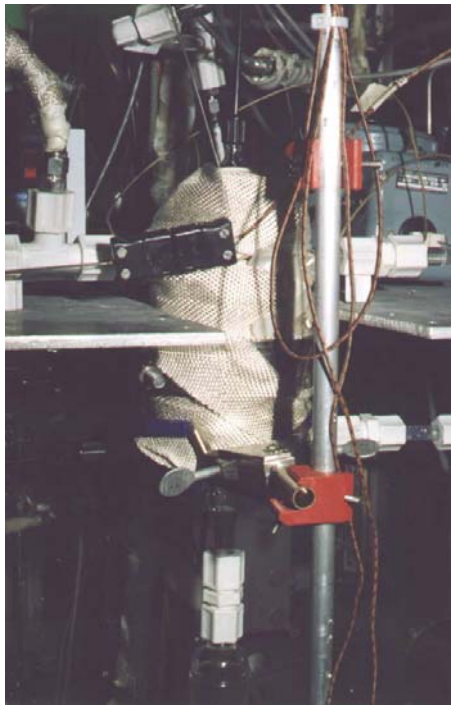
[a] 15–min test as versus 30 min for other data.

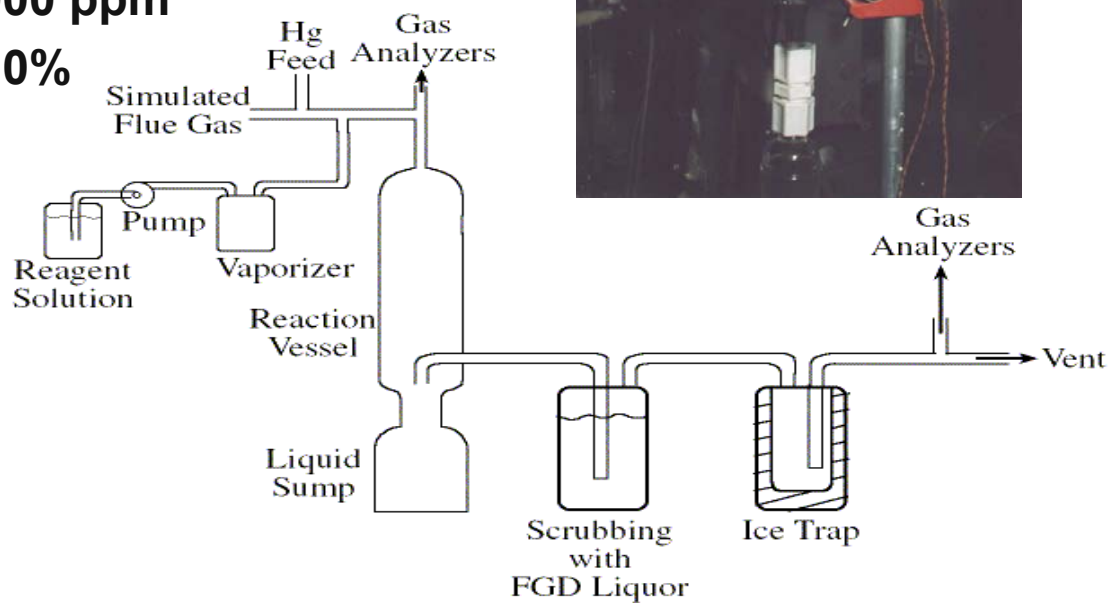
Follow-on Research Focused on Chloric Acid and Combined Hg/NO_x Removal

- **Testing conditions included:**
  - **Chloric acid and chlorine as reagents**
  - **Injection of reagents into simulated flue gas as a spray or as a vapor**
  - **Different residence times between injection and scrubbing**
  - **Different reagent concentrations**
  - **Different flue-gas temperatures**
  - **Different flue-gas compositions in terms of species and their concentrations**

Typical Experimental Conditions Included:

- **Temperature** — **300 - 350°F**
- **Residence time** — **8 - 12 sec**
- **Gas composition**
  - **Mercury** — **50 µg/m^3**
  - **NO** — **250 - 400 ppm**
  - **SO_2** — **0 - 1900 ppm**
  - **CO_2** — **11 - 20%**
  - **O_2** — **0-1%**





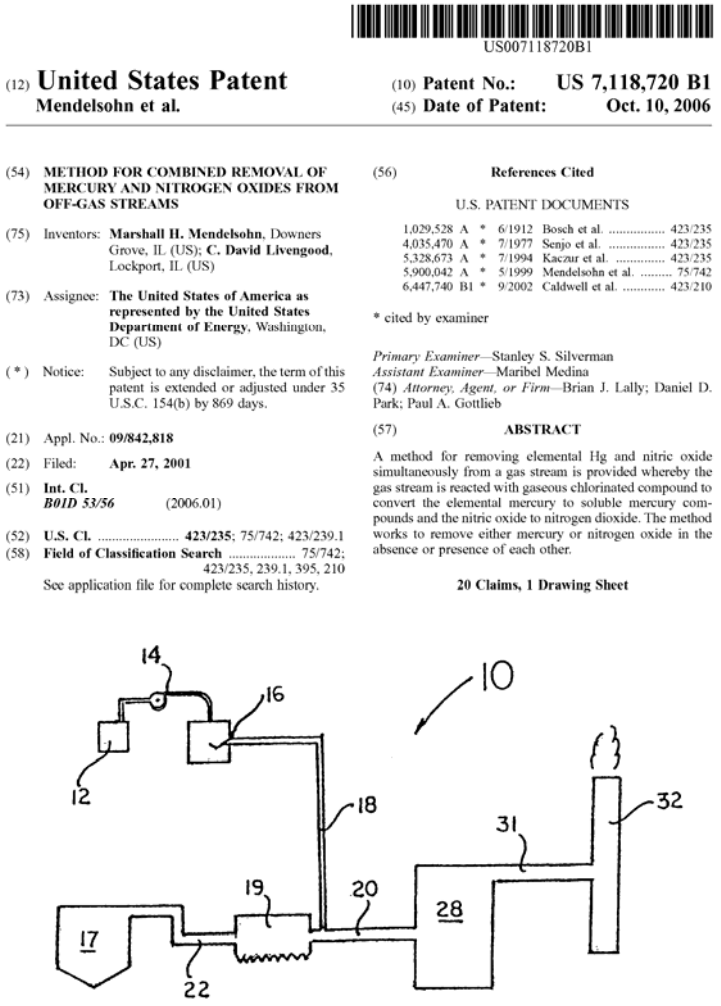
Typical Results with Chloric Acid Injection Show Potential for Combined Hg/NO_x Removal Even in the Presence of SO_2

Gas Composition	NO Removal	Hg Removal
$N_2+Hg^0+CO_2+NO$	80%	~100%
$N_2+Hg^0+CO_2+NO+SO_2$	92-97%	87%

- SO_2 degraded Hg^0 removal with chlorine, but had little effect with chloric acid
- Removal of Hg^0 was enhanced by the presence of NO while the same effect was not observed with chlorine as reagent
- Higher gas temperatures in the reaction zone improved both Hg and NO removals

Research Results Provided the Basis for a Recent Patent

- **METHOD FOR COMBINED REMOVAL OF MERCURY AND NITROGEN OXIDES FROM OFF-GAS STREAMS**
- **U.S. Patent 7,118,720; Oct. 10, 2006**
- **Marshall H. Mendelsohn and C. David Livengood**
- **ABSTRACT:**
  - **A method for removing elemental Hg and nitric oxide simultaneously from a gas stream is provided whereby the gas stream is reacted with gaseous chlorinated compound to convert the elemental mercury to soluble mercury compounds and the nitric oxide to nitrogen dioxide. The method works to remove either mercury or nitrogen oxide in the absence or presence of each other.**



US007118720B1

(12) **United States Patent**
Mendelsohn et al.

(10) **Patent No.: US 7,118,720 B1**
(45) **Date of Patent: Oct. 10, 2006**

(54) **METHOD FOR COMBINED REMOVAL OF MERCURY AND NITROGEN OXIDES FROM OFF-GAS STREAMS**

(75) Inventors: **Marshall H. Mendelsohn**, Downers Grove, IL (US); **C. David Livengood**, Lockport, IL (US)

(73) Assignee: **The United States of America as represented by the United States Department of Energy**, Washington, DC (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 869 days.

(21) Appl. No.: **09/842,818**

(22) Filed: **Apr. 27, 2001**

(51) **Int. Cl.**
B01D 53/56 (2006.01)

(52) **U.S. Cl.** **423/235**; 75/742; 423/239.1
(58) **Field of Classification Search** 75/742; 423/235, 239.1, 395, 210
See application file for complete search history.

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5,900,042	A *	5/1999	Mendelsohn et al.	75/742
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* cited by examiner

Primary Examiner—Stanley S. Silverman
Assistant Examiner—Maribel Medina
(74) *Attorney, Agent, or Firm*—Brian J. Lally; Daniel D. Park; Paul A. Gottlieb

(57) **ABSTRACT**

A method for removing elemental Hg and nitric oxide simultaneously from a gas stream is provided whereby the gas stream is reacted with gaseous chlorinated compound to convert the elemental mercury to soluble mercury compounds and the nitric oxide to nitrogen dioxide. The method works to remove either mercury or nitrogen oxide in the absence or presence of each other.

20 Claims, 1 Drawing Sheet

Partners Are Being Sought to Collaborate on Larger-Scale Testing and Development of the Process

- **Pilot-scale testing is needed to:**
  - **Confirm process performance in actual coal-combustion flue gas**
  - **Identify any reagent handling or materials issues**
  - **Refine the promising preliminary economic estimates**
  - **Evaluate any effects on system by-products**

- **For further information, contact:**

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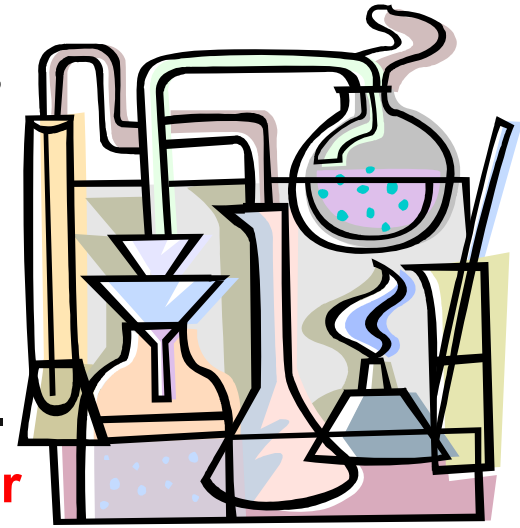
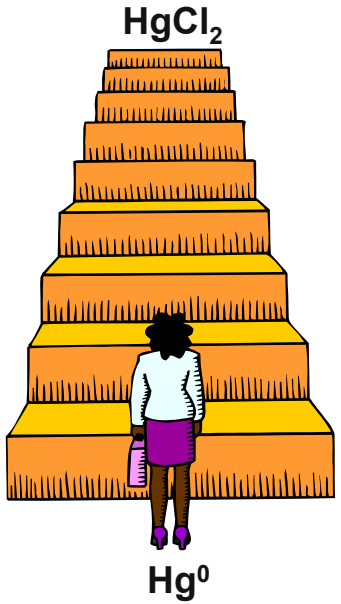
Work at Argonne and Elsewhere Focused Attention on the Role of Hg Chemistry in Control Processes



- 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.
- The review focused on chemical mechanisms for the homogeneous gas-phase chemistry of Hg^0 with Cl_2 and HCl.
- We searched the technical literature back to 1907, assembling the most relevant documents publicly available, and critically reviewing over 300 pages of material.

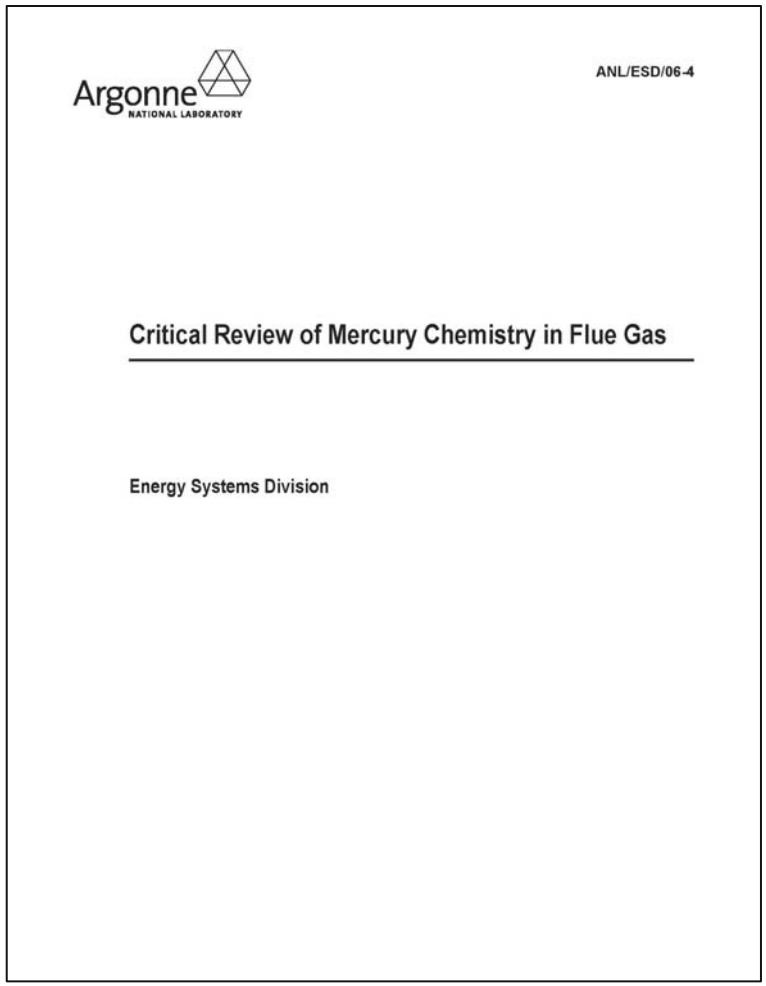
The Review Revealed Both Significant Gaps and Progress

- Early papers gave widely varying results for mercury/chlorine reaction kinetics
- Later work confirmed a slow gas-phase reaction
- Several mercury oxidation mechanisms have been proposed, including a widely used 8-step 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 have been added to better fit experimental observations



A Topical Report Detailing the Review Is In Press and Will be Available Soon

- **Summaries and citation data are provided for the literature that was reviewed**
- **Significant developments are identified**
- **Trends are analyzed and needed information is pointed out**
- **To request a copy, please leave a business card or contact**
  - **C. David Livengood; 639-252-3737; dlivengood@anl.gov**


Argonne NATIONAL LABORATORY

ANL/ESD/06-4

Critical Review of Mercury Chemistry in Flue Gas

Energy Systems Division

Additional Work Has Focused on the Chemistry Involved in:

- **The emission of elemental mercury from wet scrubbers following the capture of oxidized mercury species. Sulfur species such as sulfite/bisulfite appear to play a key role, but other factors can also influence the process.**

- **Oxidation of elemental mercury in passing through the filter cake in a baghouse. Metal species such as Fe_2O_3 and CuO may be important in this phenomenon, but there is not a clear relationship with fuel chemical analyses.**

Acknowledgments

- The authors wish to acknowledge the help and support provided by the U.S. Department of Energy, Office of Fossil Energy, which supported this work through the National Energy Technology Laboratory (NETL). In particular, we want to thank Bruce Lani and Thomas Feeley of the NETL for their support, as well as Scott Renninger who was formerly with NETL and now is with Babcock & Wilcox.