

**OHIO COAL DEVELOPMENT OFFICE
ANNUAL PROJECT ABSTRACT
AS OF DECEMBER 2004**

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| <p>1. PROJECT SPONSOR:
(entity name/ mailing address)
University of Dayton Research Institute
300 College Park
Dayton, OH 45469</p> | <p>2. PROJECT MANAGER/TITLE:
Philip H. Taylor, Ph.D.
Distinguished Research Scientist</p> |
| <p>3. OCDO GRANT NO. B4.11</p> | <p>4. PHONE: (937) 229-3604
EMAIL: Taylor@udri.udayton.edu</p> |
| <p>5. PROJECT TITLE: Kinetic Studies of Mercury Removal in Bituminous and Sub-bituminous Coals</p> | |
| <p>6. PROJECT TERM FROM: 1 Sept. 2004</p> | <p>TO: 30 Sept. 2005</p> |
| <p>7. PROJECT UPDATE xxx --OR--</p> | <p>FINAL REPORT _____</p> |
| <p>8. BUDGET:</p> | |

<u>CO-SPONSOR'S NAME</u>	<u>COST-SHARE</u>
OCDO	\$79,839
University of Dayton	\$27,259
US-EPA	\$24,000
_____	\$ _____
_____	\$ _____
TOTAL PROJECT VALUE:	\$131,098

ABSTRACT

It would be desirable to be able to predict the speciation of Hg in utility exhaust streams to more effectively manage the air quality impacts from coal utilization for electricity generation. Of particular interest is a better understanding of the differences in elemental mercury (Hg⁰) emissions from the combustion of different coal ranks, e.g. bituminous vs. sub-bituminous coals. The goal of this four-year project is to study the chemical transformation of elemental mercury in the post-combustion zone of coal combustion systems. The focus will be Hg chlorination.

The ultimate goal of this study is to reconcile the following controversial issues regarding Hg chlorination: 1) homogeneous Hg chlorination at near ambient temperatures is questionable and likely result from catalytic surface effects (Mamani-Paco and Helble, 2000), and 2) higher concentrations of gaseous HCl or Cl₂ than those found in coal combustion gases are likely required for significant Hg oxidation to occur by homogeneous reactions alone and heterogeneous reactions are necessary to account for experimental observations. Recent modeling results from Niksa, et al. (2001) of the post-combustion oxidation of Hg indicate that the only channel that oxidized Hg⁰ at an appreciable rate was Hg + C + M → HgCl + M. The primary production channel for HgCl₂ was HgCl + Cl₂ → HgCl₂ + Cl. Kinetic simulations predict that the

concentration of atomic chlorine in a cooling combustion gas is rapidly reduced by interconversion with HCl and Cl₂. The lower concentration of atomic chlorine and the potential variability in the rate coefficient for reaction with Hg⁰ at lower temperatures may result in “frozen” Hg⁺² concentrations corresponding to equilibrium values around 530°C. The gas-phase kinetics to be examined in the proposed program will provide improved insight for predicting the formation of water-soluble mercuric chloride at temperatures associated with the post-combustion regions of coal-fired power plants.

Galbreath and Zygarlicke (2000) have recently presented an excellent review of the status of elemental mercury transformation in coal combustor flue gas. Mercury chlorination is assumed to be the dominant Hg transformation mechanism. Other potential mechanisms involve Hg interactions with ash particle surfaces where reactive chemical species, catalysts, and active sorption sites are available to convert Hg⁰(g) to Hg²⁺X(g) as well as Hg⁰(g) and Hg²⁺Cl₂(g) to Hg(p). The proposed four-year program will initially focus on gas-phase processes. Our main emphasis, however, is to thoroughly examine heterogeneous Hg transformation processes.

9. OVERVIEW OF PROJECT & OBJECTIVES:

The goal of this four-year project is to study the chemical transformation of elemental mercury in the post-combustion zone of coal combustion systems. The focus will be Hg chlorination. Specific questions to be addressed for the current year include:

1. Reaction of Hg⁰ with chlorine is suspected to be an important pathway for the oxidation of Hg in post-combustion systems. What are the rates of reaction for conversion of Hg⁰ to HgCl and then to HgCl₂? What are the products of each reaction? What competing reactions are present?
2. What are the effects of surfaces on the rate of Hg chlorination? Do activated carbon, unburned carbon, and fly ash influence the rate of Hg chlorination? How do the product distributions vary in the presence of these surfaces?
3. What other Hg transformation processes are important in post-combustion environments of utility systems?

Three inter-related tasks are being conducted. Task 1 will continue our study of the gas-phase rates of Hg chlorination using a laser-induced fluorescence technique. Task 2 will continue our study elucidating the products of these gas-phase reactions at low pressures using a selective photo-ionization, time-flight mass spectrometer. Task 3, a new task, will investigate the influence of different surfaces on the product distributions of Hg chlorination/oxidation reactions using an atmospheric pressure tubular flow reactor coupled to gas chromatographic/mass spectrometric detection. Experimental temperatures will encompass the following post-combustion units in a coal fired power plant: economizer (315-400°C), selective catalytic reduction for NO_x (330°C), and precipitator (150°C).

Experimental temperatures for the proposed kinetics study will encompass the following post-combustion units in a coal fired power plant: economizer (315-400°C), selective catalytic reduction for NO_x (330°C), and precipitator (150°C).

10. WORK TO DATE & CONCLUSIONS:

Task 1 – A manuscript summarizing the results of this study is in the process of being cleared by the US-EPA for submission to *Chemosphere*. We anticipate online submission in January or February of 2005.

Task 2 - The experimental system set-up was completed and the system is currently being diagnosed. The light emitted from the hollow cathode lamp is guided to ionization region of ToF (between repeller and extractor plate) through quartz tubing. A lithium fluoride (LiF) window was initially installed to prevent gas discharge from the lamp to ToF system. It was later found that ionization efficiency of Hg and HgCl₂ is significantly reduced if any window is applied to isolate discharge gas from the lamp. The lamp was, therefore, installed without isolation windows and

we are currently investigating the optimum condition to ionize mercury species. The system shows good response for organic species, but needs refinement to obtain good response from Hg species. The heated transfer line and Hg filtration system at the exhaust line is functioning well. The installed Hg monitoring badges indicate that Hg release to the environment is below detection limits ($80 \mu\text{g}/\text{m}^3\cdot\text{hr}$).

Task 3 - The reactor for homogeneous and heterogeneous Hg oxidation reaction study under atmospheric condition is currently under construction. The reactor front end system consists of flow controllers and plumbing for the quantitative introduction of elemental Hg, chlorinated species, and other oxidized flue gas species. Elemental mercury (Hg) and oxidized Hg such as HgCl_2 , Hg_2Cl_2 , and HgO will be monitored continuously using a continuous emission monitoring system, the OhioLumex-915 MiniCEM (see photo to the left). This CEM is based on the analytical approach of thermo-catalytic conversion and atomic absorption for detection of elemental and oxidized Hg with Zeeman background correction. The use of a multipath call combined with a dry converter provides high Hg sensitivity with no interference from the combustion gas matrix. The detection limit of Hg species is $2 \text{ ng}/\text{m}^3$, which are 3 orders of magnitude lower than our experimental condition.



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11. PLANS FOR COMING YEAR:

Task 1 – We hope to have the kinetic measurements accepted for publication during

the 2005 calendar year.

Task 2 - The goal of these *in situ* product measurements will be to confirm the reaction products that have been identified in our modeling calculations. We then plan to publish the results as a companion to the kinetic results in task 1.

Task 3 – The initial goals of this task are identification of important Hg oxidation mechanisms among variety of homogeneous and heterogeneous reactions using the RA-915 CEM Hg analyzer, and the quantitative analysis of reaction products using our existing Saturn 2000 GC/MS/MS.

12. HIGHLIGHTS/ACCOMPLISHMENTS:

Task 1 has been completed. A journal article has been prepared and will be submitted for publication during the first few months of 2005.

13. ARTICLES/PRESENTATIONS:

A manuscript entitled "LP/LIF Study of the Formation and Consumption of Mercury (I) Chloride: Kinetics of Mercury Chlorination" has been prepared for publication in the journal *Chemosphere*. The corresponding author is Philip H. Taylor. Co-authors are Rajesh Mallipeddi and Takahiro Yamada. A presentation was given at the *2004 Ohio Air Quality & Coal Research Symposium* summarizing the results of Task 1. The title of the presentation was "Kinetic Studies of Mercury Removal." The talk was given by Philip H. Taylor. Co-authors were Rajesh Mallipeddi and Takahiro Yamada.