Subtask 2.7 - Mercury Capture on Solid Surfaces and Aerosols

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SUBTASK 2.7 – MERCURY CAPTURE ON SOLID SURFACES AND AEROSOLS

1.0 INTRODUCTION

Determining the fly ash properties responsible for the capture of mercury in coal-fired power generation systems is key to understanding and controlling mercury emissions in these systems. Several capture mechanisms and interactions may be possible, such as condensation, chemical adsorption, physical adsorption, chemical bonding, and amalgamation. The chemical nature of the exposed surfaces and the amount of surface area are likely to affect the amount of mercury capture, so both of these parameters must be explored. Since much of the fly ash surface area is concentrated on submicron particles, the interaction of mercury with submicron particles needs to be evaluated. Another possible explanation of mercury capture on fly ash is the formation of amalgams with other metal species that may be present in the fly ash; if this is true, amalgamation may be a viable control technology.

2.0 OBJECTIVES

The project objectives are to relate mercury capture by fly ash to chemical and physical properties of the fly ash, determine mercury associations with submicron aerosols, evaluate mercury capture on metal sorbents, and relate experimental results to predictions based on state-of-the-art models.

3.0 SCOPE OF WORK/RESULTS

The work has been divided into three activities that cover the entire scope of work.

3.1 Activity 1 – Mercury Capture Mechanisms on Coal Combustion Fly Ash

3.1.1 Introduction

Variable capture of mercury on coal combustion fly ash has been noted in previous Energy & Environmental Research Center (EERC) research projects. While mercury capture on fly ash has been attributed to the carbon contained in fly ash, the capture efficiency noted in our studies does not correlate with the loss on ignition values (LOI). LOI is commonly used as an indicator of carbon content in fly ash, although other attributes of the fly ash may also contribute to the LOI value. It is expected that carbon plays a significant role in mercury capture on fly ash, but other mechanisms may also contribute to this capture. A key aspect of this activity will be the evaluation of carbon content and forms.

3.1.2 Task Goal and Objectives

The goal of this task is to determine what, if any, role the inorganic fraction of coal combustion fly ash plays in sorption of elemental mercury. The supporting objectives include

determination of types of carbon present in coal combustion fly ash and the relative mercury sorption capacity or affinity of the various carbon types present in the fly ash samples evaluated.

3.1.3 Work Plan

The work plan for this activity is summarized as follows:

- Select three fly ash samples generated in controlled conditions that have exhibited varying amounts of mercury capture over a range of LOI. It is anticipated that the three samples will represent a bituminous coal fly ash, a subbituminous coal fly ash, and a lignite fly ash.
- Develop and apply a selective characterization protocol to determine mercury associations in the selected fly ash samples. This protocol is expected to include sample separation by particle size, density, carbon fraction, and/or magnetic separation. Bulk chemistry of all bulk samples and fractions will be determined. The bulk sample and fractions are expected to be characterized by optical microscopy to evaluate surface chemistry of the materials and to determine the types of carbon present. Surface area and mineralogy will also be included in the characterization protocol.
- Results of the characterization will be correlated to determine trends in the occurrence of mercury relative to various parameters such as isotropic or anisotropic coke, crystalline carbon, magnetic minerals, surface phenomenon, and other candidate properties.
- Following determination of the likely mechanism or mechanisms for the mercury capture, several additional "clean" utility-generated fly ash samples will be selected from the Coal Ash Properties Database for testing and verification of the proposed mechanism. These bulk ash samples will be characterized for selected parameters from the protocol summarized. The samples will then be subjected to a gas flow containing elemental mercury. Following this laboratory-scale test, the samples will be analyzed for mercury to determine mercury capture.

3.1.4 Work Plan Modifications

Minor modifications to the work plan were made in the preliminary phases of this activity. Three fly ash samples were identified from previous work for the laboratory investigations; however, it was determined that only two of these samples sorbed mercury under the laboratory conditions selected for this activity. In order to obtain an additional sample for completion of this activity, six additional fly ash samples were screened for mercury sorption behavior. From all samples screened, two lignite and one subbituminous fly ash sample generated in the EERC pilot-scale facilities and four utility-generated bituminous fly ash samples with relatively high carbon content were identified as good candidates for laboratory study. One lignite fly ash, the subbituminous fly ash, and two of the bituminous fly ash samples were selected. Two bituminous samples were selected because two primary types of carbon were identified in the bituminous fly ash samples, which are well represented in the two samples selected.

Because of the one additional sample selected, it was decided to limit the separation and following sorption experiments to carbon-ash separations. This will provide information on mercury sorption in the carbon fractions and the inorganic fractions of fly ash from three ranks of coal.

3.1.5 Accomplishments

The laboratory apparatus for mercury sorption/desorption experiments was assembled and trial runs were performed to determine sample requirements, flow rates, and optimum mercury concentrations for fly ash experiments. Two lignite and one subbituminous fly ash samples generated in the EERC pilot-scale facilities and four utility-generated bituminous fly ash samples with relatively high carbon content were initially identified as good candidates for laboratory study. Preliminary mercury sorption screening tests were performed on these pilot-scale and utility-generated fly ash samples, and results were correlated with LOI results. LOI results were used as a preliminary estimate of carbon content in the sorbing and nonsorbing fly ash samples. Without exception, nonsorbing fly ash samples exhibited low loss on ignition.

Results of this screening process provided information to further limit the number of samples for complete investigation. A set of four samples was selected based on these preliminary experiments and the results of evaluation of carbon types present in available high-carbon fly ash samples. One lignite fly ash, the subbituminous fly ash, and two of the bituminous fly ash samples were selected. Two bituminous samples were selected because two primary types of carbon were identified in the bituminous fly ash samples, which are well represented in the two samples selected.

Total mercury content of the selected samples was performed. The bituminous samples had been separated previously into high- and low-carbon fractions. The lignite ash and the subbituminous ash were submitted for separation which was accomplished by means of a dry, triboelectrostatic separation process at the University of Kentucky, Center for Applied Energy Research. The result of this separation was a set of nine fractions for each sample. The highest and lowest carbon fractions will be used for the remaining sorption experiments. The fractions of interest for these two samples and the high- and low-carbon fractions from the bituminous coal ash samples were submitted for total mercury content and carbon analysis. Mercury sorption experiments continue on both bulk samples and high- and low-carbon fractions.

3.2 Activity 2 – Mercury Associations with Submicron Aerosols

3.2.1 Goal

The goal of this activity is to measure mercury removal associated with known distributions of laboratory-generated submicron aerosols produced from pure water-soluble substances with the TSI Tri-Jet aerosol generator in addition to submicron SO₃ (which forms sulfuric acid mist) generated using the EERC SO₃ generator.

3.2.2 Scope of Work

Known concentrations of vapor-phase elemental mercury and mercuric chloride will be spiked into a heated aerosol chamber using permeation tubes. The TSI Tri-Jet aerosol generator or EERC SO₃ generator will be used to generate submicron aerosols with particle-size distributions measured with the TSI scanning mobility particle sizer. Because of limitations of the SemTech mercury analyzer with particulate-loaded sample gas, wet chemistry methods (tris buffer or EPA Method 101A) will be used to measure inlet and outlet mercuric chloride. The Environmental Process Monitor (EPM) mercury analyzer will be used to measure elemental mercury. Outlet filter samples will also be analyzed for mercury. Independent variables investigated are mercuric chloride and elemental mercury species, aerosol type, aerosol concentration, temperature, and residence time.

3.2.3 Results

A heated aerosol chamber was constructed of glass and used to evaluate elemental mercury removal for three water-soluble aerosols and SO₃. With inlet elemental mercury concentrations of 40–50 µg/m³, aerosols of KCl, NaNO₃, and Na₂SO₄ in concentrations of approximately 150 µg/m³ and 500 µg/m³ did not show any elemental mercury removal across the aerosol chamber at room temperature (approximately 70°F) or elevated temperatures of 250°F. No removal was seen with inlet elemental mercury concentrations of 35–40 µg/m³, 115°F, and submicron SO₃ at concentrations of 15 and 70 ppm. No size distributions or filter analyses were done since no mercury removal was measured.

Spiking and recovery of mercuric chloride at the bench scale has been developed under separate EERC mercury investigations. It is known that glass surfaces must be kept at a minimum of 250°F to prevent significant mercuric chloride deposition. At this time, results are not entirely satisfactory, and it is not yet confirmed if the data discrepancies are due to operational problems with the permeation tubes, system temperatures, the on-line mercury analyzers and corresponding conversion systems, or wet chemistry methods. Work in the aerosol chamber will begin by establishing a mercuric chloride blank across the chamber. If the blank tests are acceptable, mercuric chloride tests using the water-soluble aerosols and SO₃ will be completed by the first week of February 1997.

3.3 Activity 3 – Metals for Mercury Capture

3.3.1 Methodology

Three metals—zinc (Zn), tin (Sn), and gold (Au)—in granular form were used to determine their suitability for the capture of mercury vapor. A total of 25 experiments were performed where the metal granules were packed in a filter bed through which a gas stream of nitrogen and mercury was passed at different temperatures. Up to 30 g of filter material was used per experiment, and the particle size varied from 0.06 to 6 mm. The experiments with Au used Au-coated silica sand with 0.125% to 1.0% Au by mass, while Zn and Sn were solid granules, reagent-grade 99.8% or higher. The Au-coated silica filters were packed in a quartz tube (0.6-mm inside diameter) and the Zn and Sn in a Teflon tube (13-mm inside diameter).

The total gas flow rates were controlled between 4 to 20 L/min, and mercury concentrations were varied between 15 to 80 $\mu\text{g}/\text{m}^3$ of mercury to simulate elevated mercury emissions in a flue gas. Elemental mercury vapor was generated by a calibrated permeation tube at a constant temperature of 82.4°C, and its output was controlled by nitrogen flow in the slipstream. An on-line SemTech mercury analyzer was used to determine the breakthrough curves for the various filters. Breakthrough behavior was determined for temperatures of the percolating gas at 70°, 90°, 100°, and 200°C.

3.3.2 Results

Zinc, tin, and gold are known for their solubility in mercury, which enables them to form amalgams. The formation of these intermetallic compounds is the mechanism, which is being tested in this study, by which mercury vapor is captured by metals.

The solubility of the three selected metals in mercury is as follows:

Metal	Solubility in Mercury (Atomic Percent)
Au	0.14
Sn	1.26
Zn	6.23

Although zinc and tin have solubilities that are an order of magnitude higher than gold, Au was the only metal to effectively capture mercury vapor from a gas stream. Because of kinetic limitations and/or oxidation of Zn and Sn under ambient conditions, these metals were not able to capture any mercury in detectable amounts. The very rapid breakthrough of mercury through zinc and tin filters is shown in Figure 1. A breakthrough of mercury vapor through the filter was evidenced within 30 seconds at all temperatures between 70° to 200°C. The 30-second lag corresponds to the residence time of the gas in the tubing between the filter tube and the SemTech mercury analyzer. The breakthrough did not appear to be affected by the surface area of the granules in the filter. Four different granule diameters in the Zn and Sn filter showed the same breakthrough behavior. Breakthrough for zinc and tin filters can, therefore, be assumed to be instant and independent of temperature and surface area.

An attempt was made to reduce the oxidation of fresh metal surfaces by acid-rinsing the granules ("etching") prior to filter packing. Acid-rinsed Zn granules were dried with nitrogen gas at 200°C flowing through the filter tube for several hours to inhibit surface oxidation. Even after this pretreatment, mercury capture could not be detected, and breakthrough of the zinc filter was instant.

Gold, on the other hand, showed excellent mercury sorption capacity. This was expected, based on the mechanisms of several mercury vapor detectors, but quantification of mercury sorption of gold-coated silica remained to be determined. A filter packed with 0.5 g of this material, containing 0.125% Au by mass, was able to delay mercury breakthrough by more than 30 minutes.

Figure 1. Hg breakthrough of zinc and tin at 70° and 200°C.

The flow rate in these experiments was approximately 4 L/min and sample volume was 1.7 cm³, which corresponds to a residence time in the filter of less than 0.03 seconds.

Figure 2 shows the effect of gold concentration on the breakthrough behavior at 70°C. Silica sand with Au loadings of 0.125%, 0.25%, and 1.00% by mass, indicate an increasing sorption capacity with increasing gold loading. Note that this relationship is not linear and that optimal gold concentration for this material will probably be in the range from 0.25% to 0.5% Au. Mass calculations indicate that a sorbent-to-mercury ratio of 75 is sufficient to effectively capture mercury vapor from gas streams at 70°C. For a 1% gold concentration, the sorbent-to-mercury ratio increases to approximately 300 for the same temperature. These ratios compare favorably with activated carbons that require 1000 to 10,000 sorbent-to-mercury ratios.

Figure 3 shows the breakthrough curves for the same materials at a gas temperature of 200°C. At this increased temperature, the times to breakthrough are approximately a factor of 1.5 less than at 70°C, and breakthrough occurs within 15 to 30 minutes. At 200°C, the sorbent-to-mercury ratio for 0.125% Au filter is 150 and for a 1.00% Au filter is 300.

The effect of temperature on mercury sorption on a 0.125% gold-coated silica is illustrated in Figure 4. At 200°C, mercury appears behind the filter after 15 minutes, while at 70°C, the gold filter holds the mercury for over 35 minutes. The curves shown in this figure have an increasing slope with increasing temperature. This is believed to be caused by temperature-dependent diffusion through the filter, subsequently affecting the sorption of mercury in a nonlinear manner.

Figure 2. Hg breakthrough of gold-coated silica sand at 70°C.

Figure 3. Hg breakthrough of gold-coated silica sand at 200°C.

Figure 4. Hg breakthrough of gold-coated silica sand at 0.125% gold mass loading.

3.3.3 Conclusions

- Zinc and tin, in purest metallic form available, do not capture vapor-phase mercury, even though their solubility in mercury is among the highest for metals. The formation of intermetallic bonds (Zn-Hg and Sn-Hg) is hampered by slow kinetic processes.
- Gold is capable of capturing mercury from a gas stream very effectively. Even in the form of gold-coated sand at 0.125% Au loading by mass, filters were able to retain mercury at a sorbent-to-mercury ratio from 75 to 150 in the temperature range of 70° to 200°C.
- Sorption by gold is very fast even at elevated temperatures. A residence time of 0.03 seconds in a filter with 0.005 g of gold was sufficient to retain mercury for over 1 hour.
- The effects of other gases in addition to nitrogen on mercury capture by gold needs to be investigated, as well as the regeneration of the filter material.
- Possibilities of combining metals in mercury filters should be investigated. Small amounts of gold may be sufficient to capture mercury, while metals with higher solubilities could be used to retain larger amounts of captured mercury and prolong filter life.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
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Page 1 of 2

1. Program/Project Identification No. DE-FC21-93MC30097		2. Program/Project Title TASK 2.0 AIR QUALITY ASSESSMENT AND CONTROL					3. Reporting Period 10-1-96 through 12-31-96									
4. Name and Address Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000							5. Program Start Date 01-12-93									
							6. Completion Date 12-31-97									
7. FY 96/97	8. Months or Quarters Quarters	b. Dollar Scale	1st JAN	FEB	MAR	2nd APR	MAY	JUN	3rd JUL	AUG	SEP	4th OCT	NOV	DEC		
9. Cost Status a. Dollars Expressed In Thousands																
10. Cost Chart																
Fund Source		Quarter				Cum. to Date	Tot. Plan									
		1st	2nd	3rd	4th											
DOE	P	0	66	67	67	200	200									
	A	0	18	22	37	77										
	P															
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	P															
	A															
Total P		0	66	67	67	200	200									
Total A		0	18	22	37	77										
Variance		0	48	45	30	123										
P = Planned A = Actual																
Total Planned Costs for Program/Project \$200						c. Cumulative Accrued Costs										
Planned						0			66			133			200	
Actual						0			18			40			77	
Variance						0			48			93			123	

11. Major Milestone Status	Units Planned	
	Units Complete	
2.7 Mercury Capture Mechanisms on Solid Surfaces and Aerosols	P	
	C	
2.8 Mercury Speciation and Capture in Scrubber Solutions	P	
	C	
2.9 Improved Methods for Chlorine and Flourine in Coal	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks	
13. Signature of Recipient and Date <i>Smith 2/7/97</i>	14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Subtask 2.7	Mercury Capture Mechanisms on Solids & Aerosols				
a	Task Initialization - procure supplies, determine establish test matrix	3/96	8/96	1	
b	Perform bench-scale experiments	8/96			
c	Evaluate data and perform additional tests if necessary	10/96			
d	Submit draft topical report and an article for publication	12/96			
Subtask 2.8	Wet-Scrubber Effects on Mercury Speciation				
a	Modify mercury bench-scale unit. Construct and shake down bench-scale scrubber	3/96			
b	Complete bench-scale tests	6/96			
c	Complete data reduction and evaluation	8/96			
d	Submit draft topical report and an article for publication	12/96			
Subtask 2.9	Improved Methods for Cl and F in Coal				
a	Evaluate ASTM proposed pyrohydrolysis method	5/96		2	
b	Compare pyrohydrolysis method to oxygen bomb combustion method	11/96			
c	Submit draft topical report and an article for publication	12/96			
1	Delayed due to late finalization of Cooperative Agreement				
2	Project withdrawn due to partial funding of the Cooperative Agreement				

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