ELEMENTAL MERCURY REMOVAL USING A WET SCRUBBER*

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ABSTRACT

Mercury (Hg) is a toxic metal that is emitted into the environment by both natural and human activities. Acute and chronic exposure to mercury and methyl mercury in humans results in central nervous system damage, kidney damage, and even death. Although some Hg emission sources have been regulated, coal-fired utilities have not been. In anticipation of federal regulations on mercury emissions from coal-fired power plants, Argonne National Laboratory (ANL) has designed a flue gas simulation system to study the removal of elemental mercury. The simulated flue gas enters the system and combines with the inlet mercury vapor (from a calibrated permeation tube), carried by nitrogen gas. This combined gas continues past the flow meter and the pressure gage to the reactor inlet. Inside the reactor chamber, the flue gas is sprayed with NOXSORB®, a chloric acid solution, which reacts with elemental mercury. The amount of reaction (oxidation) of elemental mercury is important since mercury in an oxidized form is highly soluble. In this form, the Hg can be picked up downstream by a wet scrubber from fossil-fuel burning utilities.[1-4]

Experiments on mercury removal from flue gases have been conducted at ANL, with the participation of a senior design team from Purdue University Calumet. Temperature variations ranging from room temperature to 350°F have been studied. Other parameters, such as the concentration of NOXSORB®, were also tested. Furthermore, pump speed and sprayer droplet sizes of the NOXSORB® solution were studied.

A literature survey on the current and proposed mercury control legislation, along with the existing control technologies, has been performed as part of the senior design project. With guidance from ANL, an understanding of the simulation system has been developed. This information has been used to determine the mass transfer. Another literature survey was performed on the reaction kinetics of mercury. The information obtained was used to postulate probable behavior of elemental mercury in flue gas.

The experimental results obtained at Argonne will be related to existing wet scrubber technology to determine the economic feasibility of mercury removal. A cost per pound of mercury analysis will be utilized.

INTRODUCTION

Concerns about mercury emissions into the atmosphere are rapidly increasing. Results of numerous studies are shedding light on what is still a relatively little known subject. Regulations are already in place for limiting mercury emissions from municipal solid waste (MSW) boilers. However, coal-burning electric utilities, which are a major source of mercury emissions, have not been regulated. As part of an effort to control mercury emissions, the U.S. Congress mandated that the U.S. Environmental Protection Agency (EPA) conduct an extensive study on mercury emissions

One of the objectives of this paper is to look specifically at coal burning utility plants in an effort to assess current mercury control systems and to evaluate potential designs for new mercury emission controls. One of the first major problems encountered with attempts to control Hg emissions from coal-fired electric utilities is that after combustion, mercury is a volatile trace element that exists as a vapor passing through the existing control devices and straight into the atmosphere. In fact, there is still considerable uncertainty about the types and concentrations of individual mercury compounds in the flue gas. According to Huang et al., "the lack of information... makes a credible risk assessment impossible...".[5]

The U.S. Department of Energy has responded to these concerns by sponsoring research at Argonne National Laboratory (ANL) on elemental mercury emissions from coal-fired utilities. ANL has developed an elemental mercury removal process utilizing existing wet limestone scrubbers and NOXSORB®, a chloric acid solution.[7] Additional solutions of the reagent NOXSORB® are injected into the flue gas stream prior to scrubbing. The intent is to oxidize elemental mercury into a more soluble form that can then be captured in the scrubber slurry. This paper details the experimental methodology, mass balance, and the chemical reactions involved.

APPARATUS AND PROCEDURE

A design schematic of the lab-scale Hg^0 removal process utilizing an ultrasonic atomizer is shown in Figure 1. As depicted in the diagram, the simulated flue gas enters the system and combines with the N_2 gas stream that is used as a carrier gas for the elemental mercury. This combined gas stream continues past the flow meter and the pressure gage to the reactor inlet. The reactor simulates the ductwork prior to scrubbing in a full-size operation. The residence time in the chamber is ranged from 6 to 10 s according to Livengood.[6] Inside the reactor chamber, the flue gas is bombarded with reactant by an ultrasonic atomizer. The atomizer mists the reactant for an even distribution within the reactor and simulates a co-flow scrubber process. The gas then enters the bubbler where the oxidized mercury is captured. The Hg^0 levels found in both the bubbler and the sump indicate the amount of Hg^0 removed from the flue gas.

NOXSORB® Injection

The NOXSORB® is sprayed into the flue gas stream prior to scrubbing on a vertical length of simulated ductwork. The NOXSORB® is injected into the reactor in the middle of the chamber with the ultrasonic atomizer. The mist is assumed to have a linear flow to simplify the analysis of the spray. The volumetric gas flow rate of the combined gases into the reactor is approximately 6 L/min. This volumetric gas flow rate is assumed constant throughout the system. However, adjustments are necessary during the test cycle to maintain steady flow.

The reactor chamber diameter is 3 in. and the gas lines to and from the reactor have inside diameters of 3/8 in. The residence time is the time that a single particle of NOXSORB® would spend inside the reactor with the flue gas. The average distance for the residence time is 3.75 in., which is one-half the total height of the reactor.

Lab Scrubber

The lab scrubber is a bubbler type. The lab scrubber is filled with 200 mL of a water and sodium hydroxide (NaOH) solution. This solution imitates the process found in industrial scrubbers. The velocities of the bubbles reflect the residence time, which directly affects the amount of Hg^0 removal obtained.[7]

Laboratory Procedure

The following simplified procedure was used to conduct the experiments utilizing the atomizer at room temperature and elevated temperatures:

1. The flue gas constituents are fed into the system ,and the constituents are measured by using Beckman instruments. Typical flue gas concentrations are 14 - 16% CO_2 with a 99.5% purity, 300-450 ppm NO with 99.0% purity, and 650-750 ppm SO_2 with 99.98% purity.
2. The Teflon® gas tubing is then heated for high-temperature tests.
3. A solution of NOXSORB™ and distilled water is prepared and primed into the atomizer. Liquid flow rates through the atomizer were varied, depending on the desired flow rate.
4. A solution of approximately 0.3 g of sodium hydroxide (NaOH) in 200 mL of distilled water is prepared as the bubbler liquor. This liquor mimics the liquor found in the typical wet scrubber.
5. An elemental mercury permeation tube is placed in a N_2 gas stream at 70°C. This tube is calibrated to release 3.57 µg of Hg/15 min at 70°C.
6. Typical gas flow rates for the nitrogen-mercury stream are 4.8 L/min; the typical gas flow rate for the total gas stream, including the nitrogen-mercury, is 6.0 L/min.
7. The NOXSORB® is injected into the gas stream for 15 min.
8. Liquid samples from both the sump and bubbler were saved for each test and analyzed for mercury content.
9. Mercury analyses were performed by a standard cold-vapor atomic absorption spectrophotometric method (U.S. EPA Method 7470A, SW-846). The estimated accuracy for this method is ±10% or ±0.02 µg/L, whichever is greater.

RESULTS AND DISCUSSION

Mass Analysis

Initial baseline tests were performed to validate the absence of residual mercury in the simulation system. These tests used water as the oxidizing agent. Then, a series of tests was run to determine the removal effectiveness of NOXSORB® injection at room temperature. The lab system set-up was analyzed for mass

balance of the Hg^0. The Hg^0 is carried by a nitrogen (N_2) gas stream and combined with the simulated flue gas. The simulated flue gas temperatures were both ambient and heated to simulate actual temperatures. The reagent solution, NOXSORB®, was then injected into the gas stream to oxidize the Hg^0. The sump condensate and the bubbler solution were collected and analyzed for Hg^0 content. The following mass analysis demonstrates this process. A description of the system components is presented as product-in equals product-out. The first law of thermodynamics, which states that mass is constant, is applied in Equation 1.

$$(mercury)+(flue\ gas)+(reagent) = (condensate)+(scrubber\ content)+(exit\ gas) \qquad (1)$$

The total amount of Hg^0 collected from the sump and the bubbler was calculated for each test. This total was then divided by the total Hg^0 calibration of $3.57\mu g$, which indicates the percentage of Hg^0 captured. Trace amounts of oxygen (O_2) were also present in the flue gas; however, it was not added to the system. Since O_2 would only improve the oxidation of Hg^0, the actual O_2 found in typical flue gas content would not retard the results obtained from this process.

The mass balance of the process is analyzed by using the experimental results in the *Data Analysis* section of this report. Exact stoichiometric chemical equations regarding the system components are beyond the scope of this project. Therefore, a simplified analysis of the important reactions is discussed in the Chemical Reaction Analysis section of this report.

Data Analysis

Figure 2 represents the Hg^0 and Nitric Oxide(NO) removal results obtained for gas streams of N_2 and CO_2 at room temperature. The Hg^0 removal effectiveness increases with increasing NOXSORB® concentrations. The test with the lowest concentration of NOXSORB® removed only 9% of the mercury and an immeasurable amount of NO. Therefore, at room temperature, the process would be considered too expensive to remove a substantial amount of mercury.

It was then decided to conduct experiments at increased flue-gas temperatures to investigate removal effectiveness under real-world conditions at a typical coal-burning power plant. The results for the elevated temperature testing using the ultrasonic atomizer are shown in Table 1. A significant increase in the Hg^0 removal was demonstrated using the 1% solution, with minimal NO removal. The 4% concentration of the NOXSORB yielded very good results; however, even at these concentrations, the economics are still unreasonable. These results indicate that the elevated temperatures

significantly aid in the removal efficiency, even at low NOXSORB concentrations.[6]

A new method was implemented to introduce the NOXSORB® into the gas stream. The process description is proprietary; however, the results from these experiments are found in Table 2. These results are significant because of the very low volumes of NOXSORB® required for maximum Hg^0 and NO removal efficiencies. These tests will be duplicated in the future to verify the results. The addition of sulfur dioxide did not significantly affect the removal efficiencies of this new process.

Table 3 compares the results of ambient and high-temperature tests for which the ultrasonic atomizer was used. The 1% NOXSORB® concentrations, in conjunction with the elevated temperature, removed 51% more Hg^0 and 30% NO. The 4% NOXSORB® concentration test for the elevated temperature removed 66% more Hg^0 and 77% more NO. Therefore, it appears that the elevated temperatures required less NOXSORB® solution for a significant increase in the removal efficiencies.
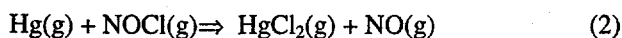
Chemical Reaction Analysis

To make an assessment of the behavior of elemental mercury in flue gas from coal-fired power plants, all the variables must be defined. The first step is to determine the gases produced when coal is combusted. According to Hall et al., all combustion processes generate basically the following gases: N_2, O_2, H_2O, CO, and NO_x. They add that other gases (such as SO_2, HCl, Cl_2, H_2S, and NH_3) are also present; however, their concentrations are dependent on the type of coal combusted and the temperature conditions of the furnace.[8]

According to Mendelsohn and Livengood, the reactions of NO and NOXSORB® produce hydrochloric and nitric acids, which may cause the improved Hg removal when NO is in the gas stream. An explanation is that since nitric acid dissolves liquid mercury, the formed nitrous/acid may oxidize the Hg^0. They add that nitric acid is commonly used and in combination with HCl in the laboratory protocols for the analysis of mercury compounds and in cleaning laboratory equipment of mercury residues. This conclusion is supported by Lindberg and Stratton when they show that trends in mercury speciation may suggest that peak concentrations of NO_x and SO_2 correlated with peak concentrations of reactive gaseous mercury (RGM).

In addition, a different pattern of behavior was found for solutions containing chlorine or chlorine compounds. Chlorine solutions showed no dependence on concentration when nitric oxide and sulfur dioxide were absent, indicating that the mercury-chlorine reaction is probably slow without the presence of a catalyst. Addition

of nitric oxide to the gas stream greatly increased the amount of Hg^0 removal.

This increase in the removal may have been due to the formation of an intermediate compound, such as nitrosyl chloride (NOCl), which could react rapidly with the Hg^0.

$$Hg(g) + NOCl(g) \Rightarrow HgCl_2(g) + NO(g) \qquad (2)$$

ANL's conclusion for the reaction of Hg in the presence of NO is that NOCl probably reacts faster with Hg^0 than does Cl_2. It is believed that Hg^0 reacts faster with Cl_2 if there is a catalyst (such as NO) or, as mentioned before, a product of the NO and NOXSORB® reaction. More research is required to determine the exact mechanisms involved.[8-14]

Mercury Removal Efficiency

According to the Olin Corporation, the cost of NOXSORB® is approximately \$0.7/lb. Assuming that NOXSORB® has the same density of water (0.997 g/cm^3), the NOXSORB® pounds per one liter can be calculated by using Equation 3.

$$(0.997 \ g/cm^3) \times (1 \ cm^3/0.001 \ L) \times (0.0022046 \ lb/g)$$
$$= 2.198 \ lb/L \qquad (3)$$

The cost per pound of mercury removed is estimated at \$25,000 for optimal conditions. The goal of this project was to achieve a \$50,000 cost per pound of mercury removed with 90% removal rate. The process achieved less than half of the proposed cost per pound. Therefore, the new method is economically feasible. Additional savings can be obtained from the NO removal.

Capital costs associated with the system will vary depending on the existing system components already in place. The system must be custom-engineered on the basis of the following: size of boiler; type of coal combusted; flue-gas volume; auxiliary equipment; and federal, state, and local regulations. The associated maintenance and operating costs are also not yet identifiable, as the system components are not yet established. Many other factors must be considered in the implementation of this process (i.e., waste management, solution regeneration, scrubber slurry contamination, corrosion of the system components, and monitoring of the mercury emissions).

CONCLUSION

Wet limestone scrubbers were found to be the most common flue gas desulfurization (FGD) process used. FGD systems have proven to be the most effective in reducing Hg^0 emissions (up to 50%). Design parameters for a typical coal-fired utility FGD scrubbing system were based on the wet limestone, droplet-type scrubber system with a reactant introduced prior to scrubbing and after the electrostatic precipitator.

An understanding of the lab-scale mercury removal process developed by ANL was established. The physical attributes of the lab processes were identified, and the process flow diagram was developed. The necessary equations required to analyze the duct injection and the bubbles in the lab scrubber were developed. Finally, a simplified lab procedure was developed.

Additional analysis was performed for the mass balance of the mercury in the system. The majority of the mercury was captured in the sump condensate, with most of the remainder collecting in the slurry. The chemical reaction kinetics were investigated, and the evidence suggests that the majority of the mercury reactions occur in the vapor phase. The results of the NOXSORB® experiments showed the addition of NO appears to enhance mercury removal, suggesting that there is an intermediate reaction.

Finally, a simple economic analysis was performed on the basis of the amount of NOXSORB® necessary to accomplish a significant mercury removal from flue gas. This process, which used a new method of NOXSORB® injection, removed 100% of the mercury emissions (80% of the NO emissions) at a cost of \$24,500 per pound of mercury removed.

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TABLE 1 Elevated Temperature Test Results

NOXSORB® CONCENTRATION (%)	Hg^0 REMOVAL (%)	NO REMOVAL (%)
1	60	30
4	95	83

TABLE 2 New Method Test Results

FLUE-GAS COMPOSITION	Hg^0 REMOVAL (%)	NO REMOVAL (%)
$N_2 + Hg^0 + CO_2 + NO$	100	80
$N_2 + Hg^0 + CO_2 + NO + SO_2$	87	92-97

TABLE 3 Comparison of Ultrasonic Atomizer Tests

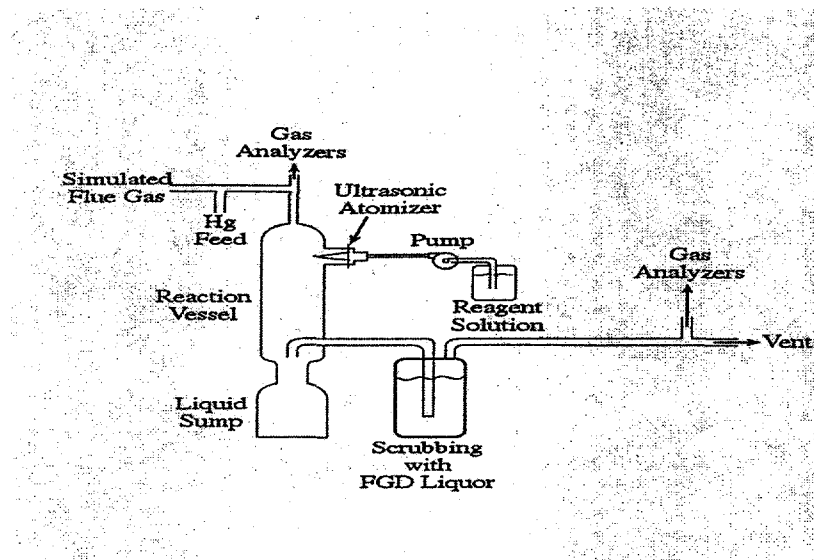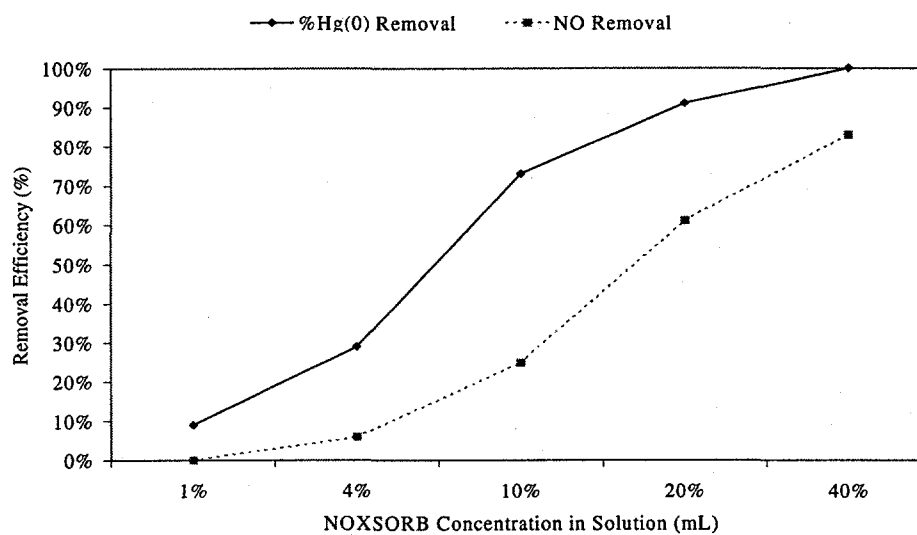| NOXSORB® CONCENTRATION (%)	Hg^0 REMOVAL (%)		NO REMOVAL (%)	
	AMBIENT	350°F	AMBIENT	350°F
1	9	60	--	30
4	29	95	6	83

FIGURE 1. Lab Process Flow Diagram.

FIGURE 2. Hg⁰ and Nitric Oxide Removal Efficiencies.