ENHANCEMENT OF MERCURY CONTROL IN

FLUE-GAS CLEANUP SYSTEMS

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INTRODUCTION

The control of anthropogenic sources of mercury is receiving increased legislative and regulatory attention at both the state and federal level due to the potential for deleterious environmental and human health effects. Those sources include coal-fired boilers, but field studies have shown that current flue-gas cleanup (FGC) systems are relatively ineffective in controlling elemental mercury, which is often a major component of the total emissions. This paper summarizes research at Argonne National Laboratory which is focused on techniques to enhance the capture of elemental mercury and integrate its control into existing FGC systems.

Dry sorbents could be utilized in a variety of process configurations, including injection into the flue-gas ductwork upstream of a particulate-matter collector. Argonne has evaluated the mercury-capture performance of a number of commercial and developmental sorbents (primarily activated carbons). However, data reported from field tests with activated carbon have shown that high sorbent to mercury ratios are needed for effective collection. In order to reduce the costs for duct injection, recent Argonne research has focused on low-cost sorbents produced through chemical treatment of inert substrates, and has demonstrated that performance comparable to higher priced activated carbons can be achieved.

Both laboratory and field tests have shown that very little elemental mercury is captured in a wet scrubber system due to the low solubility of that species. To enhance the ability of wet scrubbers to capture mercury, Argonne has studied improved mass transfer through both mechanical and chemical means, as well as the conversion of elemental mercury into a more soluble species that can be easily absorbed. Current research is investigating the roles of several halogen species either alone or in combination with typical flue-gas components such as sulfur dioxide (SO_2) and nitric oxide (NO) in the oxidation of mercury to form compounds that are easily scrubbed from the flue gas.

EXPERIMENTAL FACILITIES

Argonne's laboratory facilities for FGC research include a fixed-bed reactor system for studying dry sorbents, a complete wet scrubber system, and a spray-dryer/fabric-filter system. Supporting facilities include a system that can provide known concentrations of elemental mercury in a gas stream, a gas-supply system capable of blending synthetic flue gas from bottled gases, on-line gas-analyzers, and data loggers. More detailed descriptions of all of the systems can be found in References 1 and 2.

MASTER

DISCLAIMER

The mercury feed-gas preparation system consists of a permeation tube containing elemental mercury, a constant-temperature water bath, and a carrier-gas supply (usually nitrogen). The design capacity of the system is 20 L/min of gas with mercury concentrations of up to 100 µg/m³. This feed gas can be used alone or combined with gases from a separate blending system that can supply typical concentrations of oxygen (O_2), carbon dioxide (CO_2), SO_2, NO, and nitrogen dioxide (NO_2).

Gas-phase measurements of elemental mercury are made using a gold-film mercury-vapor analyzer. The range of the instrument is 0 to 999 µg/m³ with a sensitivity of 3 µg/m³ and an accuracy of ± 5% at 100 µg/m³. Measurements of the mercury concentrations in liquid samples are made using a standard cold-vapor atomic absorption spectrophotometric method (EPA Method 7470A, SW-846) with an estimated accuracy of ± 10%.

The fixed-bed reactor is constructed of glass, and is 4 cm in diameter and 14 cm in height. A glass frit is positioned in the lower section to support materials placed inside the reactor. To avoid fluidization of the bed materials, the feed gas enters the reactor from the top and exits at the bottom. Silica sand is used as a diluent for the sorbent in order to avoid agglomeration and channeling. To maintain a uniform temperature during experiments, the reactor is immersed in a fluidized-bed, constant-temperature sand bath.

Wet scrubbing experiments have been conducted both in the lab-scale wet scrubber and in a system consisting of three 150 mL bubblers connected in series. The glass scrubber column has an inside diameter of 7.6 cm and an active height of nearly 53 cm. It is normally operated in a countercurrent mode with the flue gas entering at the bottom. The scrubber is constructed of several interchangeable sections so that it can be configured as a flooded column (no internals), a four-stage disc and donut column, or an intermediate combination. For most of the experiments, the combination mode was used with the lower part of the column left open to accommodate packing.

DRY SORBENT DEVELOPMENT

Earlier research focused on commercial, activated-carbon-based sorbents, and investigated the capacity of those sorbents as a function of factors such as temperature, particle size, and mercury concentration.[1] For those carbons, by far the best removal results were obtained with a sample that was commercially treated with about 15 wt% sulfur. The success of the sulfur-treated carbon is thought to be based on a combination of physical adsorption and chemical reactions that produce mercury sulfide. This suggests that chemical additives producing other compounds, such as mercury chloride, might also be beneficial for removal. To explore this possibility, another carbon sample, which previously gave essentially no removal, was treated with calcium chloride ($CaCl_2$) in the ratio of about 6:1 by weight. The treated carbon gave excellent removals and actually performed better than the sulfur-treated carbon.

In order to develop lower-cost alternatives to activated carbon, the research focus was shifted to chemical pretreatment of several high-surface-area and/or low-cost mineral substrates. Tests of the materials in the as-received condition gave moderate mercury removals for a molecular sieve sample and essentially no removals for volcanic pumice or vermiculite. However, experiments with volcanic pumice treated with $CaCl_2$, potassium iodide (KI), and sulfur produced significant removals. At 70°C, the sulfur-treated sorbent gave 100% removal for over an hour, while the iodide-impregnated sorbent gave 100% removal for a few minutes followed by a decrease in removal that appeared to level out at about 30%. The chloride-impregnated sorbent behaved somewhat differently, with the removal gradually increasing to a final value of about 30%. Figure 1 indicates that at 70°C the performance of the sulfur-treated pumice was comparable to that of the sulfur-impregnated carbon, even though the weight-percent sulfur was less than half as much. As part of this work, a new method for applying the sulfur has been developed, which utilizes a more "environmentally friendly" solvent for the sulfur than the one used in commercial processes.

2

In the earlier work, flue-gas temperature was shown to be a particularly important variable in mercury capture. In order to explore the effects of temperature on the treated sorbents, additional tests were run at a temperature of 150°C. The iodide-impregnated sample behaved very similarly at the two temperatures. However, the sulfur treatment that was so effective at the lower temperature was found to be relatively ineffective at the higher temperature. This may represent a loss of sulfur or a change in the form of the sulfur, but this issue has not yet been resolved. Tests at intermediate temperatures indicate a rapid decrease in sorbent effectiveness above approximately 110°C.
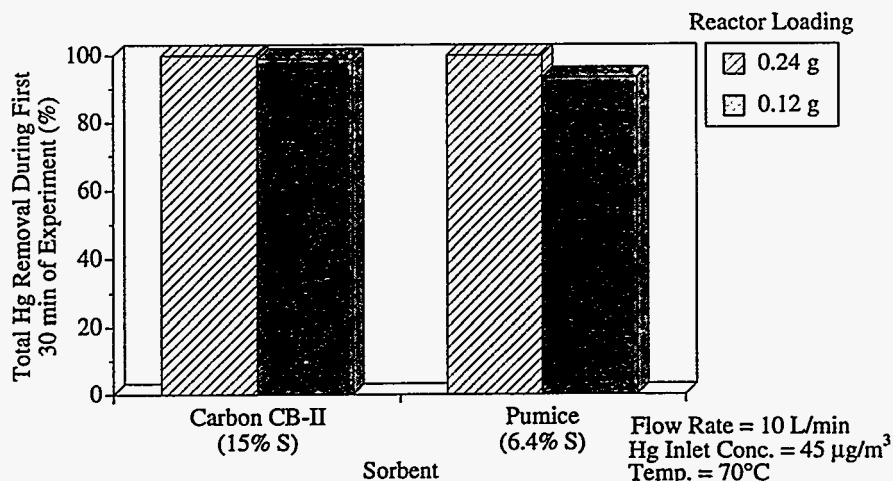

Figure 1. Mercury Capture by Sulfur-Treated Carbon and Pumice.

WET SCRUBBING RESEARCH

Previous laboratory research[3] and field tests[4] have indicated that wet scrubbing is not likely to be an effective control measure for elemental mercury. In an effort to promote greater mercury capture through changing its chemical form, tests were conducted with several additives that combine strong oxidizing properties with relatively high vapor pressures. Tests with minimal gas-liquid contacting in the scrubber gave mercury removals as high as 100% and indicated that the removal reactions were occurring in the gas phase above the scrubber liquor. However, tests with the addition of SO_2 to the gas stream showed the additives to be very reactive with that species as well, which could result in excessively high additive consumption in order to realize effective mercury control.

Next, scrubbing tests were conducted with a new combination of oxidizing chemicals, NOXSORB™, which is a product of the Olin Corporation. Typical feed-gas compositions included 1000 ppm SO_2, 200 ppm NO, 15% CO_2, and 33 µg/m³ Hg. While interferences from the additional gas species emerged as an issue in the operation of the mercury analyzer, the readings still indicated very good removal of elemental mercury. In a batch test with a dilute (4%) solution of the as-received NOXSORB™ concentrate, an outlet reading of zero was obtained for Hg over a period of about 24 min. During that period, the NO outlet concentration decreased rapidly to near zero and then rose gradually to where it was almost equal to the inlet value. The breakthrough in the Hg concentration (the point at which the concentration rises above zero) appeared to coincide with the point at which the NO concentration leveled off. The apparent correlation between NO and Hg removals from this and other tests implied that the mercury may have been reacting with a product or intermediate of the NO removal process. A moderate degree of SO_2 removal was also observed during the time the NOXSORB™ solution was circulating.

In order to further explore the interactions between additives and various gas species, a series of experiments using bubblers was conceived. In these experiments, the first bubbler (in a series of three) contained 150 mL of a solution of the chemical under investigation, while the second and third bubblers contained only water. Analyses of the liquids in the bubblers were used to determine the degree of

3

mercury capture. Baseline tests verified that essentially no Hg was removed in this apparatus when only distilled water was used in the first bubbler.

Iodine Solutions

A commercial 0.100 N iodine solution was diluted to make up various iodine concentrations. For a solution of 125 ppb iodine in bubbler #1, more than 90% of the inlet Hg was found in the bubbler solutions when only N_2 and Hg were in the feed-gas stream. When O_2 and CO_2 were added to the gas mixture, Hg capture was reduced to about 6%. When either NO or SO_2 (or both) were added to the gas mixture, the amount of Hg found in the bubbler solutions went either to zero (for NO and for NO plus SO_2) or close to zero (~1% for SO_2).

Earlier tests in the scrubber indicated that the most likely Hg removal mechanism was a rapid gas-phase reaction between iodine vapors and elemental Hg, probably yielding mercuric iodide. However, some of the Hg found in bubbler #1 may be from a liquid-phase reaction at the gas-liquid interface. A published report on the reaction of iodine in solution with dissolved Hg stated that "the rate was too fast to measure".[5] Without further modeling studies and knowledge of the rate constants (no experimental data on the gas-phase reaction of Hg with iodine could be found in the literature), we cannot determine how much of each reaction (gas phase versus liquid phase) is responsible for the Hg removal. However, it is clear that the presence of other gases readily interferes with this reaction. Whether this interference is caused only by reaction of iodine with the other gaseous components, or whether another mechanism is responsible for the interference cannot be determined from these tests. In any case, iodine would not seem to be an attractive option for oxidation of elemental Hg in the presence of gases other than nitrogen.

Chlorine Solutions

Solutions of molecular chlorine (Cl_2) are more complex than those of iodine because of the tendency for Cl_2 to disproportionate in aqueous solution to hypochlorous acid and chloride ions. Due to the various equilibria involved, detectable amounts of Cl_2 will exist both in the gas and liquid phases. Recent modeling work has assumed the rate constant for the gas-phase reaction of Hg with Cl_2 to be very small.[6] On the other hand, laboratory experiments have shown conflicting results. Some workers have found this reaction to be slow[7] while others have found it to be relatively fast.[8] Still other work has shown the reaction of Hg with Cl_2 to be surface catalyzed.[9] It appears from these conflicting results that one must be very careful in interpreting data for this reaction. Our data suggest that for Hg in gas mixtures containing only O_2 and N_2, the rate of reaction between Hg and Cl_2 is not fast, because not much change in Hg removal was observed with increasing chlorine concentration.

However, addition of NO to the feed-gas mixture had a positive effect on the amount of Hg transferred to the liquid phase. An explanation may be that NO reacts with Cl_2 to yield nitrosyl chloride (NOCl). This reaction has been described in the literature and appears to occur rapidly at room temperature.[10] No literature reference to the reaction of NOCl with elemental Hg could be found, but NOCl has been found to oxidize mercurous chloride to mercuric chloride as well as oxidizing elemental zinc and copper.[11] Our conclusion is that NOCl probably reacts faster with Hg than Cl_2 does.

When SO_2 was added to the feed-gas mixture, the Hg removal was much lower at the lower chlorine concentrations than when SO_2 was not present. However, at the highest chlorine concentration studied, the Hg removal performance with SO_2 present actually slightly exceeded performance without SO_2. Since sulfite ions reduce molecular halogens to their corresponding halides, the presence of SO_2 should not increase the oxidation of Hg by Cl_2. The improvement in Hg removal with chlorine concentration may simply be due to the presence of an excess of Cl_2 that swamps the reaction between dissolved bisulfite

4

(from absorbed SO_2) and Cl_2 and/or hypochlorite ions in solution. A better understanding of this behavior will require more detailed testing.

Chloric Acid Solutions

Chloric acid solutions ($HClO_3$) were prepared from a concentrated NOXSORB™ solution, which had a nominal composition of 17.8% $HClO_3$ and 22.3% sodium chlorate. The primary vapor-phase species above these solutions is thought to be chlorine dioxide (ClO_2). However, ClO_2 is very reactive and readily photolyses to Cl_2 and O_2. Also, in the presence of moisture, ClO_2 can produce a number of different

Figure 2. Mercury Capture as a Function of Additive Concentration and Gas Composition.

chlorine oxyacids, such as $HOCl$, $HClO_2$, etc. Therefore, a large number of different species may be present in the vapor above an $HClO_3$ solution. To the best of our knowledge, the reaction of Hg with either ClO_2 or chlorate anions has not been studied previously.
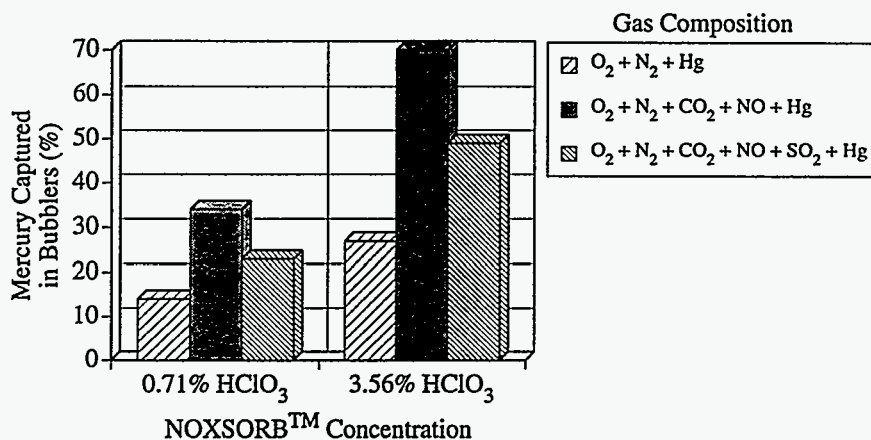
As shown in Figure 2, a five-fold increase in $HClO_3$ concentration produced about the same relative change in Hg removal for the three different feed-gas mixtures studied. In each case, the Hg removal was about a factor of two higher with the higher concentration $HClO_3$ solution. Again, the gas mixture that contained NO showed a higher Hg removal than the gas mixture without NO. This result is similar to that observed with chlorine solutions. However, a mechanism different than that proposed for Cl_2 is probably responsible. It has been postulated that reaction of NO with NOXSORB™ solutions produces hydrochloric and nitric acids among its products.[12] Since nitric acid dissolves liquid elemental Hg, this gaseous reaction by-product may cause the improved Hg removal when NO is present. The presence of SO_2 in the feed-gas stream reduced the Hg removal by about 30% from the level without SO_2 (but with NO), and contrary to the behavior observed with chlorine, it appears as though the mechanism that causes a reduction in Hg removal when SO_2 is present *cannot* be overcome with higher $HClO_3$ concentrations. This result again points to the possibility that a mechanism different from Cl_2 oxidation of Hg is operating for these $HClO_3$ solutions. These tests with $HClO_3$ suggest that the gas-phase reaction of Hg with nitric acid might be rapid and should be examined further.

CONCLUSIONS

Chemical treatment of inert substrates may offer an economically attractive alternative to activated carbon for the control of mercury emissions. Among the chemicals tested thus far, there are significant differences in removal efficiency, performance as a function of temperature, and properties of the expected product compounds. Sulfur is a particularly effective treatment at lower temperatures, but further work is needed to achieve better performance at higher flue-gas temperatures. In addition, the effects on particulate-matter collection, fly ash marketability, and/or by-product disposal need to be determined.

Process concepts employing additives to alter mercury speciation prior to capture in a wet scrubber appear to be technically feasible. Interactions between various gas-phase species vary with different additives,

but clearly can be significant and, in some cases, beneficial for mercury capture. More research on the chemical mechanisms is needed to guide process design, evaluate economic feasibility, and identify potential secondary effects on scrubber operation, worker safety, waste properties, etc.

ACKNOWLEDGMENTS

REFERENCES

1. Livengood, C.D., M.H. Mendelsohn, H.S. Huang, and J.M. Wu, 1995, *Development of Mercury Control Techniques for Utility Boilers*, Proc. 88th Annual Meeting & Exhibition of the Air & Waste Management Association, San Antonio, Texas, June 18-23.

2. Mendelsohn, M.H., and J.B.L. Harkness, 1991, *Enhanced Flue-Gas Denitrification Using Ferrous•EDTA and a Polyphenolic Compound in an Aqueous Scrubber System*, Energy & Fuels, 5(2):244-247.

3. Livengood, C.D., H.S. Huang, M.H. Mendelsohn, and J.M. Wu, 1995, *Development of Mercury Control Enhancements for Flue-Gas Cleanup Systems*, Proc. EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, August 15-18.

4. Schmidt, C.E., and T.D. Brown, 1994, *Results from the Department of Energy's Assessment of Air Toxics Emissions from Coal-Fired Power Plants*, presentation at Illinois Coal Development Board Program Committee Meeting, Nov. 15.

5. Warrick, Jr., P., E.M. Wewerka, and M.M. Kreevoy, 1962, *The Reactions of Iodine in Solution with Elemental Mercury*, J. Am. Chem. Soc., *85*, 1909-1915.

6. Pleijel, K., and J. Munthe, 1995, *Modelling the Atmospheric Mercury Cycle - Chemistry in Fog Droplets*, Atmospheric Environment, *29*, 1441-1457.

7. Skare, I., and R. Johansson, 1992, *Reactions Between Mercury Vapor and Chlorine Gas at Occupational Exposure Levels*, Chemosphere, *24*, 1633-1644.

8. Skripnik, V.A., L.F. Fedorovskaya, L.I. Kravetskii, and I.M. Umanskaya, 1979, *Mechanism and Kinetics of Mercury Oxidation by Chlorine-Containing Solutions*, Zh. Prikl. Khim. (Leningrad), *52*, 1233-1237 (Engl. trans. 1169-1172).

9. Medhekar, A.K., M. Rokni, D.W. Trainor, and J.H. Jacob, 1979, *Surface Catalyzed Reaction of $Hg + Cl_2$*, Chem. Phys. Letters, *65*, 600-604.

10. Stoddart, E.M., 1944, *The Kinetics of the Reaction between Chlorine and Nitric Oxide*, J. Chem. Soc., 388-393.

11. Partington, J.R., and A.L. Whynes, 1948, *The Action of Nitrosyl Chloride on Some Metals and Their Compounds*, J. Chem. Soc., 1952-1958.

12. Kaczur, J.J., 1996, *Oxidation Chemistry of Chloric Acid in NOx/SOx and Air Toxic Metal Removal from Gas Streams*, AIChE 1996 Spring National Meeting, New Orleans, La.