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REACTIONS OF GASEOUS, ELEMENTAL MERCURY WITH DILUTE HALOGEN SOLUTIONS

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ABSTRACT

Of the trace elements known to exist in fossil fuels, mercury (Hg) has emerged as one of the greatest concerns. Mercury has been found to be emitted from combustion in at least two different chemical forms: elemental Hg and oxidized Hg compounds. Precise identification of the oxidized compounds emitted has not been accomplished to date. However, most workers in this field assume that mercuric chloride should be the predominant oxidized species. Mercuric chloride should be readily removed in a wet scrubber system because of its relatively high solubility in water. However, it has been presumed, and we have shown, that elemental Hg will pass through a wet scrubber system with little or no removal being effected. Therefore, it is important, in order to obtain a high total Hg removal, to study methods that might result in a removal of gaseous, elemental Hg from a flue-gas stream. In this regard, we have been studying the effect of dilute halogen-containing solutions on elemental Hg in gas streams of various compositions. In particular, the results of passing Hg through bubblers containing solutions of iodine, chlorine, and chloric acid are described. Mercury found in the bubbler solutions is an indication of the extent of reaction (oxidation) of elemental Hg with the halogen species, since we have found very little Hg transferred to the liquid phase when only distilled water is used in the bubblers. Results using commercial iodine, sodium hypochlorite, and NOXSORB™ solutions are presented and discussed.

INTRODUCTION

The 1990 Clean Air Act Amendments designate 189 substances as hazardous air pollutants also called "air toxics." Mercury (Hg) has emerged as one of the air toxics of greatest concern. Mercury has been found in the stack emissions from U.S. power plants [1]. Coal-fired power plants account for the vast majority of the estimated total Hg emissions from all U.S. power plants. Mercury emitted from coal-fired power plants has been found in a variety of chemical forms, including elemental Hg and oxidized Hg compounds, such as mercuric chloride [1]. Highly soluble Hg compounds, such as mercuric chloride, are assumed to be readily removed in a wet scrubber system. However, elemental Hg, because of its very low solubility in water, has been shown *not* to be captured in a laboratory-scale wet scrubber system [2]. Therefore, in order to remove elemental Hg with a wet scrubber system, an additional method must be incorporated into a typical wet flue-gas scrubbing process.

We have been studying methods to oxidize gaseous elemental Hg in a typical flue-gas environment, which includes the presence of other potentially reactive gases in the gas mixture, such as oxygen (O_2), nitric oxide (NO), and sulfur dioxide (SO_2). In this paper, we summarize results of Hg removal found by bubbling various gas mixtures containing elemental Hg through solutions of iodine, chlorine, and chloric acid. Although there are some literature references to reactions of elemental Hg with these reactants, we believe that this is the first study that also includes NO and SO_2 in the gaseous reaction mixture. Results for iodine solutions showed that a very high Hg removal was obtained only when the gas phase mixture consisted of Hg and nitrogen (N_2). When other gases were included in the feed gas mixture, the amount of Hg found in the liquid phase was drastically reduced. With chlorine solutions, a more complex behavior was observed that depended on the feed gas mixture and concentration of chlorine used. Chloric acid solutions were prepared from a commercial NOXSORB™ preparation obtained from the Olin Corporation. These solutions showed a moderate amount of Hg removal (14-27%) for the concentrations studied when only O_2 and N_2 were added to the feed gas mixture. Substantially more Hg was removed (34-70%) when NO was added to the feed gas mixture. Finally, when SO_2 was added to the mixture with NO, a moderate decrease in Hg removal from that observed with NO alone was noted (23-49%). All the results are presented and discussed more fully below.

EXPERIMENTAL SETUP AND PROCEDURES

A calibrated and certified Hg permeation tube from VICI Metronics was used as a constant source of vapor-phase, elemental Hg. The permeation tube was placed in a constant temperature water bath controlled to about ± 0.5°C. Bottled, high purity (99.998%) nitrogen gas flowed around the permeation tube to produce a gas stream with a constant concentration of elemental Hg. This gas stream was then combined with another gas stream containing nitrogen and other gaseous components, including O_2, carbon dioxide (CO_2), NO, and SO_2. Carbon dioxide was used as a carrier gas for the NO. Oxygen was used from a laboratory air line without further purification. Carbon dioxide, NO, and SO_2 were used from bottled gases without further purification. Nominal purities for these gases were as follows: CO_2, 99.5%; NO, >99.0%; SO_2, >99.98%. Gases were blended and their initial composition checked with the following Beckman instruments: O_2, Model 755 Oxygen Analyzer; CO_2, Model 864 Infrared Analyzer; NO, Model 951A NO/NO_x Analyzer; SO_2, Model 865 Infrared Analyzer. Typical concentrations of the various gas components were as follows: O_2, 5%; CO_2, 15%; NO, 250 ppm; and SO_2, 1000 ppm. After the feed gas composition had stabilized, a valve was turned to admit the gas mixture to a series of three bubblers, each containing 150 mL of solution. The first bubbler contained the solution to be studied, while the

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second and third bubblers usually contained distilled water. Commercial solutions of iodine, chlorine (sold as sodium hypochlorite), and chloric acid (sold as NOXSORB™ by the Olin Corporation) were used without further purification. Each test was performed by allowing the gas mixture to bubble through the bubblers for exactly 30 min. Liquid phase samples from each bubbler were saved for total Hg analysis. Mercury analyses were performed by a standard cold-vapor atomic absorption spectrophotometric method (U.S. EPA Method 7470A, SW-846). Mercury concentrations were determined to ± 0.02 μg Hg/L. Estimated accuracy for this method is ± 10%.

RESULTS AND DISCUSSION

The purpose of the tests described above was twofold. First, we wanted to study the effects on Hg removal from additions of the gases NO and SO_2 to a Hg-containing gas stream. Second, we wanted to learn about the Hg removal process in regard to gas phase versus liquid phase reaction mechanisms. We realized, after we began testing, that only minimal information on our second objective could be gained from these experiments. We could presume that Hg found in the second bubbler was due to gas phase reactions, assuming that liquid carryover from the first bubbler was negligible. However, the situation in bubbler #1 is more complex. From these tests, we cannot distinguish in bubbler #1 between gas phase reactions inside the gas bubble followed by rapid dissolution of products in the liquid phase, and gas-phase dissolution at the gas-liquid interface followed by rapid liquid-phase reaction.

Before tests were performed with various solutions in bubbler #1, initial baseline tests were carried out with only distilled water in all three bubblers. When no elemental Hg was added to the gas stream, no Hg was found in any of the bubbler solutions. This result demonstrates that our system is free of Hg contamination to the detection limit (± 0.02 μg Hg/L or ± 0.003 μg Hg in 150 mL of water) of the Hg analytical method described above. Such baseline tests were run periodically to ensure that no Hg contamination had built up during the course of testing described in this paper. A second baseline test was performed with Hg added to the feed gas stream, but again with only distilled water in all three bubblers. For this test, amounts of Hg barely above the detection limit (0.004-0.005 μg Hg in 150 mL) were found in each of the three bubblers. This amount of Hg may be compared with the calculated amount of Hg in the gas stream of 1.9 μg for the 30-minute test. This result shows that the amount of Hg removed in this experimental apparatus by using only distilled water is less than 0.3%. Therefore, any amounts of Hg found in the bubblers greater than this baseline amount must be from reactions of elemental Hg with components of the various solutions tested in bubbler #1.

Iodine Solutions

Commercial iodine solutions generally contain potassium iodide as a stabilizer, as well as dissolved iodine. A commercial preparation of 0.100 N iodine solution was diluted to make up various iodine concentrations. Previous experiments in our laboratory had shown that iodine solutions react rapidly with elemental Hg vapor [3] in gas streams containing only Hg and N_2. However, those tests had been performed by using only a gas-phase Hg analyzer to measure the elemental Hg concentration in both the feed and effluent gas streams. The analyzer used in those tests has recently been shown by us to be unreliable for measuring Hg in various complex gas mixtures. The tests reported here are the first ones where Hg in the liquid phase has been analyzed. Using a solution of about 125 ppb iodine in bubbler #1, we found that more than 90% of the gas-phase Hg was 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 removal was reduced to about 6%. Only one test was performed with a higher iodine concentration in bubbler #1 (~250 ppb iodine). This test, for a gas stream containing only Hg and N_2, did not give a result substantially different from the lower concentration test (~81% Hg removal). However, 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). Iodine solutions were not investigated further in these bubbler tests.

In earlier unpublished work in our laboratory, we found that the concentration of gaseous elemental Hg was substantially reduced simply by passing Hg vapors (mixed with nitrogen gas only) over an agitated iodine solution (~250 ppb). These tests showed that the most likely Hg removal mechanism was a rapid gas-phase reaction between iodine vapors and elemental Hg, probably yielding mercuric iodide. This gas phase reaction is probably why a considerable portion (~35%) of the total mercury found in the liquid phase was found in bubblers #2 and #3. However, as discussed above, we cannot exclude the possibility that some of the Hg found in bubbler #1 is from a liquid-phase reaction at the gas-liquid interface. Indeed, a published report on the reaction of iodine in solution with dissolved Hg stated that "the rate was too fast to measure" [4]. The product of the solution reaction was shown to be mercuric iodide by its ultraviolet spectrum [4]. Therefore, 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 specifically analyze how much of each reaction (gas phase versus liquid phase) is responsible for the Hg found in bubbler #1.

We conclude that the reaction of Hg with iodine is extremely rapid in the gas phase. However, 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 greater tendency of Cl_2 to disproportionate in aqueous solution to hypochlorous acid and chloride ions. Commercial chlorine solutions are sold as sodium hypochlorite because in alkaline solutions the equilibrium between Cl_2 and hypochlorite ions greatly favors the latter. Nonetheless, because of the various equilibria involved, detectable amounts of Cl_2 will exist both in the gas and liquid phases. Results for the removal of Hg by chlorine solutions appeared to depend both on the composition of the feed gas mixture and, in some cases, on the concentration of the chlorine solution. These results are presented in Table 1 and discussed below.

The results in Table 1 are given as a percentage of the total gas-phase mercury found in the liquid phase of all three bubblers; that is, we calculated the total amount of Hg in the gas phase that passes through the bubblers from the known rate of Hg generation by the permeation tube times the 30 min duration of each test. Then the total Hg in the bubblers is found by simple addition of the amounts found in the individual bubblers (in general, bubbler #3 was not analyzed for Hg unless a significant amount was found in bubbler #2). Finally, the total liquid-phase Hg is divided by the total gas-phase mercury and the result is multiplied by 100%. As can be seen from Table 1, removal of Hg in gas mixtures containing only O_2 and N_2 did not change much for different chlorine solution concentrations. Some literature data are available on the gas phase reaction of Hg with Cl_2. Recent modelling work has assumed the rate constant to be very small [5]. On the other hand, laboratory experiments have shown conflicting results. Some workers have found this reaction to be slow [6] while others have found it to be relatively fast [7]. Still other work has shown the reaction of Hg with Cl_2 to be surface catalyzed [8]. It appears from these conflicting results that one must be very careful in interpreting data for this reaction. Our data suggest that 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. Our conclusion on the gas-phase reaction of Hg with Cl_2 is that it is slow unless there is an appropriate surface available to catalyze the reaction.

For the gas mixtures containing NO and NO plus SO_2, Hg removal increased with increasing chlorine concentration. However, the rate of increase differed for the two gas mixtures studied. Addition of NO to the feed-gas mixture appeared to have a definite positive effect on the amount of Hg transferred to the liquid phase, when compared to the removals obtained with only O_2 and N_2 present. An explanation for this behavior might 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 [9]. Although we could not find a literature reference to the reaction of NOCl with elemental Hg, there was a paper which found that NOCl oxidizes mercurous chloride to mercuric chloride as well as oxidizing elemental zinc and copper [10]. Our conclusion for the reaction of Hg in the presence of NO is that NOCl probably reacts faster with Hg than Cl_2 does.

Also, as can be noted in Table 1, when SO_2 is added to the feed-gas mixture, Hg removal is much lower at the lower chlorine concentrations than when SO_2 is not present. However, at the highest chlorine concentration studied, the Hg removal performance with SO_2 present actually slightly exceeded performance without SO_2. It is well-known that sulfite ions will reduce molecular halogens to their corresponding halides. Because of this reaction, it is hard to understand how the presence of SO_2 could actually increase the oxidation of Hg by Cl_2. Perhaps the improvement in Hg removal with chlorine concentration can be understood as simply being caused by the presence of an excess of Cl_2 that swamps the reaction between dissolved bisulfite (from absorbed SO_2) and Cl_2 and/or hypochlorite ions in solution.

Plotted in Figure 1 is a graph of the fraction of Hg found in the liquid phase as a function of the logarithm of the initial chlorine concentration in bubbler #1. The data for the tests with NO and *no* SO_2 in the feed gas mixture are shown with a straight line fit, while the data for the tests with NO *and* SO_2 in the feed gas mixture are shown with a power curve fit. The curve fits are only a guide to show the difference in the removal dependencies with chlorine concentration for the two gas mixtures. A fuller understanding of this behavior will require more detailed testing.

Chloric Acid Solutions

Chloric acid solutions ($HClO_3$) were prepared from concentrated NOXSORB™ solutions. Concentrated NOXSORB™, sold by the Olin Corporation, has a nominal composition of 17.8% $HClO_3$ and 22.3% sodium chlorate. Tests with two different $HClO_3$ concentrations were performed: 0.71% $HClO_3$ (25:1 dilution of the concentrated stock solution) and 3.56% $HClO_3$ (5:1 dilution). The primary vapor-phase species above these solutions is thought to be chlorine dioxide (ClO_2). However, ClO_2 is very reactive and readily photolyzes to Cl_2 and O_2. Also, in the presence of moisture, ClO_2 can produce a number of different chlorine oxyacids, such as HOCl, $HClO_2$, etc. Therefore, a large number of different species may be present in the vapor above a $HClO_3$ solution. To the best of our knowledge, the reaction of Hg with either ClO_2 or chlorate anions has not been studied previously. Results of our tests with two different chloric acid concentrations are shown in Table 2.

From the results shown in Table 2, we first note that the change in Hg removal from a solution of 0.71% $HClO_3$ concentration to Hg removal from an $HClO_3$ solution with about a five times higher concentration is about the same for each of the three different feed-gas mixtures; that is, Hg

removal was about a factor of two higher with the higher concentration $HClO_3$ solution. Next, we note that gas mixtures which contained NO showed a higher Hg removal that the gas mixture without NO. This result is similar to that observed with chlorine solutions. However, in this case, 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 [11]. Because nitric acid dissolves liquid elemental Hg, we propose that this gaseous nitric acid by-product causes the improved Hg removal when NO is present in the gas stream. Contrary to the behavior observed with chlorine, we found that for both concentrations studied, 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. Also in contrast to the behavior observed with Cl_2 solutions, 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.

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TABLES

Table 1. Summary of Hg removal results for tests with chlorine solutions (Cl) in bubbler #1

	Hg removal from Cl solution (%)		
Feed Gas Composition	2.5 ppm Cl	250 ppm Cl	2500 ppm Cl
$O_2 + N_2$	12	14	9
$O_2 + N_2 + NO + CO_2$	19	42	60
$O_2 + N_2 + NO + CO_2 + SO_2$	0.5	14	66

Table 2. Summary of Hg removal results for tests with $HClO_3$ solutions in bubbler #1

	Hg removal from $HClO_3$ Solution (%)	
Feed Gas Composition	0.71% $HClO_3$	3.56% $HClO_3$
$O_2 + N_2$	14	27
$O_2 + N_2 + NO + CO_2$	34	70
$O_2 + N_2 + NO + CO_2 + SO_2$	23	49

FIGURE

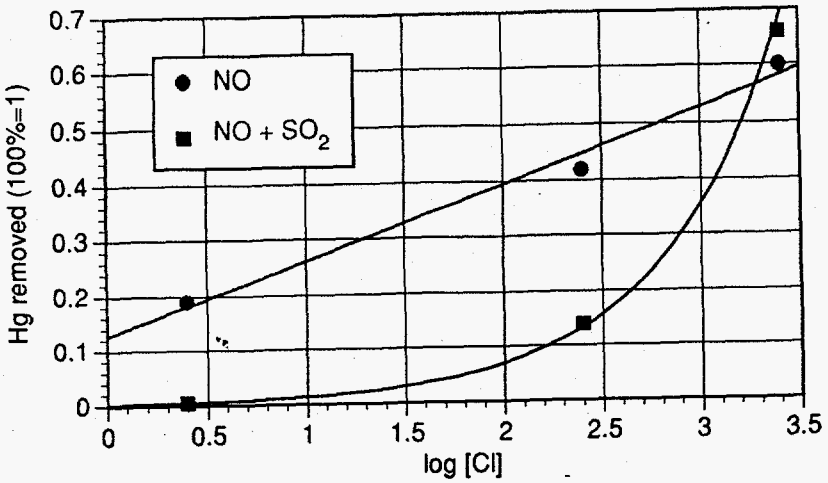

Figure 1. Dependence of Hg removal on the logarithm of the chlorine concentration for two different feed-gas mixtures

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