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Investigation of Modified Speciation for Enhanced Control of Mercury*

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Abstract

Mercury was identified as a hazardous air pollutant in Title III of the 1990 Clean Air Act Amendments. It has been singled out for particular scrutiny because of its behavior in the environment (bioaccumulation) and its potential for deleterious effects on humans and wildlife. After studying the sources of mercury in the environment, the U.S. Environmental Protection Agency has concluded that coal-fired boilers generate a significant fraction of the total anthropogenic emissions. Therefore, the agency is currently considering whether to impose mercury control requirements on coal-fired boilers in the electric utility industry. However, the costs for potential control measures (such as sorbent injection) can be extremely high.

From both an economic and operational perspective, using existing flue-gas cleaning systems for mercury control would be desirable. Wet scrubbers, in particular, have been shown to be highly effective in capturing oxidized forms of mercury. Unfortunately, a significant portion of the total mercury emissions can be in the elemental form (Hg), which is difficult to remove from flue-gas streams with existing wet-scrubber technology because of its limited solubility in water. Argonne has been investigating a concept for enhancing gaseous Hg removal in wet scrubber systems by altering the chemical form of the mercury to a water-soluble oxidized species. Initial experiments performed in aqueous bubblers revealed that up to about 70% of the Hg could be removed by using aqueous solutions of chlorine or chloric acid. From these studies, it was concluded that even higher Hg removals could be obtained if more of the reagent was made available for reaction in the gas phase. For this reason (and also to simulate a more real-world duct-injection process) a new series of tests was initiated in which an ultrasonic atomizer was used to inject small droplets of the oxidizing solutions into a reaction zone within a flowing gas stream containing Hg vapors and other typical flue-gas components. An initial series of tests, performed at room temperature, revealed that up to approximately 100% of the gaseous, elemental Hg could be transferred to the liquid phase by using chloric acid solutions under certain conditions. With a chlorine solution, up

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presence of chlorine in coal means that mercury can be found in both the elemental and oxidized forms, with the relative amounts depending on such factors as the ratio of chlorine to mercury, the gas temperature, and the gas residence time at various temperatures.² While other species are also possible and may be present in small amounts, Hg⁰ and mercuric chloride (see Table 1 for a list of selected chemical formulas) appear to be the most significant for control considerations. The huge difference in solubility between the two species is particularly important in wet scrubbing applications.

Argonne's research on mercury control has focused on improving the capture of Hg⁰. Initial experiments³ used a laboratory-scale wet scrubbing system that had been well characterized in previous work on combined sulfur dioxide/nitrogen oxides control.⁴ The feed-gas stream consisted of nitrogen containing about 40 µg/m³ of Hg⁰. The scrubber was initially operated as a partially flooded column with water, a calcium hydroxide solution, or a calcium hydroxide plus potassium polysulfide solution as the scrubbing liquor. No appreciable mercury removal was found in any of those cases.

Table 1. List of Selected Chemical Formulas

Chemical Name	Chemical Formula
Bromine	Br ₂
Carbon Dioxide	CO ₂
Calcium Hydroxide	Ca(OH) ₂
Chloric Acid	HClO ₃
Chlorine	Cl ₂
Chlorous Acid	HClO ₂
Hypochlorous Acid	HOCl
Iodine	I ₂
Mercury (elemental)	Hg ⁰
Mercuric Chloride	HgCl ₂
Nitric Oxide	NO
Nitrogen	N ₂
Nitrogen Oxides	NO _x
Nitrosyl Chloride	NOCl
Oxygen	O ₂
Sodium Chlorate	NaClO ₃
Sulfur Dioxide	SO ₂

Some improvement was found when ceramic-saddle packing was added to the scrubber, but the removals were still under 10%. More promising results were found when the packing was changed to stainless steel and used in conjunction with potassium polysulfide in the scrubbing liquor. Removals of up to 40% were obtained. However, the use of the polysulfide in FGD systems could be precluded by the fact that a very high pH is required to maintain its stability.

At that point in the program, the emphasis was shifted to the study of techniques for changing the chemical form of mercury in order to produce a more soluble species. Tests were conducted with several additives that combine strong oxidizing properties with relatively high vapor pressures (e.g., chlorine). Tests with minimal gas-liquid contacting yielded Hg^0 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 sulfur dioxide 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, tests were conducted with a chloric-acid-based chemical, NOXSORB™, which is a product of the Olin Corporation. Typical feed-gas compositions included 1,000 ppm sulfur dioxide, 200 ppm nitric oxide, 15% carbon dioxide, and $33 \mu\text{g}/\text{m}^3$ of Hg^0 . For a batch test with a dilute (4%) solution of the as-received NOXSORB™ concentrate, an outlet reading of zero was obtained for Hg^0 for approximately 24 min. During that period, the nitric oxide 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 outlet Hg^0 concentration (the point at which the concentration rose above zero) appeared to coincide with the point at which the nitric-oxide outlet concentration leveled off. The apparent correlation between the two removals indicated that the mercury could be reacting with a product or intermediate of the nitric-oxide removal process. Subsequent tests with and without nitric oxide in the flue gas again suggested that nitric oxide promoted Hg^0 removal by NOXSORB™.

The results of those tests indicated that not only could effective mercury removal be achieved via this approach, but that a combined process that also removed nitric oxide might be feasible. To explore in more detail the interactions among Hg^0 , oxidizing additives, and the various flue-gas species, a series of experiments using bubblers was designed.⁵ In those experiments, a simulated flue gas was passed through a series of three bubblers for 30 min. A solution of the reactive chemical to be tested was placed in the first bubbler, while the second and third bubblers usually contained distilled water. The degree of Hg^0 conversion was determined by comparing the amount of mercury found in the bubbler solutions with the total amount of Hg^0 fed in the flue gas. The Hg^0 concentration in the gas was typically $45 \mu\text{g}/\text{m}^3$ in nitrogen. When desired, that stream could be combined with another gas stream containing other gaseous components, such as oxygen, carbon dioxide, nitric oxide, and sulfur dioxide.

Commercial solutions of iodine, bromine, chlorine (sold as sodium hypochlorite), and chloric acid (NOXSORB™) were used without further purification. Following each test, liquid samples from each bubbler were saved for total mercury analysis by a standard cold-vapor atomic absorption spectrophotometric method.

Since it was difficult to determine the degree to which the important reactions were occurring in the gas phase, the liquid phase, or both, additional tests were performed in which the open-end inlet tube in bubbler #1 was replaced with a fritted-glass cylinder having a coarse porosity. This gas diffuser greatly decreased the size of the bubbles (by about an order of magnitude) passing through the liquid in the first bubbler, thereby increasing the available gas-liquid contact area. Thus, we expected that the results of the small-bubble tests would be more influenced by gas-liquid interactions than the corresponding large-bubble tests.

Results from the bubbler tests indicated that iodine solutions could be effective in oxidizing Hg^0 , even at very low concentrations (< 1 ppm). However, that effectiveness was lost when species other than nitrogen and Hg^0 (e.g., sulfur dioxide) were in the gas stream. For bromine, substantial conversion of Hg^0 was obtained when only oxygen and nitrogen were in the gas stream, but the addition of nitric oxide and sulfur dioxide again diminished that conversion significantly. Thus, neither iodine nor bromine is likely to be cost-effective in a commercial system.

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 removed. This increase in removal may have been due to the formation of an intermediate compound, such as nitrosyl chloride, which could react rapidly with the Hg^0 . On the other hand, sulfur dioxide depressed the Hg^0 removal, at least at lower chlorine concentrations. Nevertheless, the removal increased with chlorine concentration when either nitric oxide alone or nitric oxide plus sulfur dioxide were added to the gas stream.

Mercury removal with chloric-acid solutions also appeared to increase with increasing chloric-acid concentration regardless of gas composition. In a similar manner to chlorine, the presence of nitric oxide greatly *increased* Hg^0 removal. In this case, the important gas-phase reaction may involve nitric acid formed from the reaction of nitric oxide and chloric acid. The presence of sulfur dioxide decreased Hg^0 removal, but it remained intermediate to that with and without nitric oxide.

From a comparison of the large- and small-bubble tests, it appeared that both gas-gas and gas-liquid reactions were operating, with the gas-phase reactions involving nitric oxide becoming increasingly important as the solute concentration was raised. In that situation, some degree of nitric-oxide removal might also be obtained as part of the reaction mechanism. Soluble oxidation products could then be removed in a downstream aqueous scrubber system.

From these studies, it was concluded that even higher Hg^0 removals could be obtained if more of the reagent was made available for reaction in the gas phase. For this reason (and also to simulate a more "real-world" duct-injection process) a new series of tests was initiated in which an ultrasonic atomizer was used to inject small droplets of the oxidizing solutions into a flowing gas stream containing Hg^0 vapors and other typical flue-gas components. The results of those tests are described in the remainder of this paper.

Experimental Setup and Procedures

A simplified diagram of the experimental apparatus used for the "duct injection" tests is shown in Figure 1. The simulated flue gas flowed through a cylindrical glass duct into which a solution of either NOXSORB™ or chlorine was sprayed through an ultrasonic atomizer. This type of atomizer was used because of its ability to effectively atomize very small amounts of liquid. The duct diameter was about 3 in. and the total length was about 16 in. Reaction products were collected in both the liquid sump and the simulated FGD liquor bubbler. The second bubbler shown in the figure was used only in early tests and was empty for most of the tests. All of the tests discussed here were conducted at room temperature.

The source of Hg^0 was a calibrated and certified permeation tube from VICI Metronics, which was placed in a constant-temperature water bath controlled to $\pm 0.5^\circ\text{C}$. For the majority of the tests, the Hg^0 concentration in the gas was about $48 \mu\text{g}/\text{m}^3$. For the two tests in which only nitrogen and Hg^0 were in the gas stream, the Hg^0 concentration was about $60 \mu\text{g}/\text{m}^3$. Bottled, high-purity (99.998%) nitrogen gas flowed around the permeation tube to produce a gas stream with a constant concentration of Hg^0 . When other flue-gas components were desired, this stream was combined with another gas stream containing nitrogen and components such as carbon dioxide, nitric oxide, and sulfur dioxide. Carbon dioxide was used as a carrier gas for the nitric oxide. Carbon dioxide, nitric oxide, and sulfur dioxide were obtained from bottled gases without further purification. The nominal purities for these gases were as follows: carbon dioxide, 99.5%; nitric oxide, >99.0%; and sulfur dioxide, >99.98%.

After blending, the initial gas composition was checked with standard flue-gas analyzers from Beckman instruments: oxygen, Model 755 Oxygen Analyzer; carbon dioxide, Model 864 Infrared Analyzer; nitric oxide, Model 951A NO/NO_x Analyzer; and sulfur dioxide, Model 865 Infrared Analyzer. Typical concentrations of the various gas components were as follows: oxygen, 0-1%; carbon dioxide, 14-16%; nitric oxide, 300-450 ppm; and sulfur dioxide, 650-750 ppm.

Once the feed-gas composition was measured and stabilized, a 3-way valve was turned to divert the gas from the analyzers to the reaction duct, which had a reaction zone of about 7 in. (18 cm) extending from the ultrasonic atomizer nozzle to the gas exit. Gas flow rates were about 5 LPM for tests with only nitrogen and Hg^0 and about 6 LPM for the other tests. For a gas flow rate of 6 LPM, this resulted in an 8 sec residence time. Gaseous reactants and products were then directed to a bubbler that contained 200 mL of a 0.15 wt.% sodium hydroxide solution to remove any soluble species before exiting to the gas analyzers and a vent.

Commercial solutions of NOXSORB™ (a chloric acid/sodium chlorate solution) and chlorine (sold as sodium hypochlorite solutions) were diluted as necessary and used without further purification as the feed solutions for the ultrasonic atomizer. Liquid flow rates through the atomizer were about 13-15 mL/min. These flow conditions yield an L/G of about 16-19 GPM/1000 cfm. Any liquid remaining in the gas stream at the exit of the reaction zone was collected in the liquid sump.

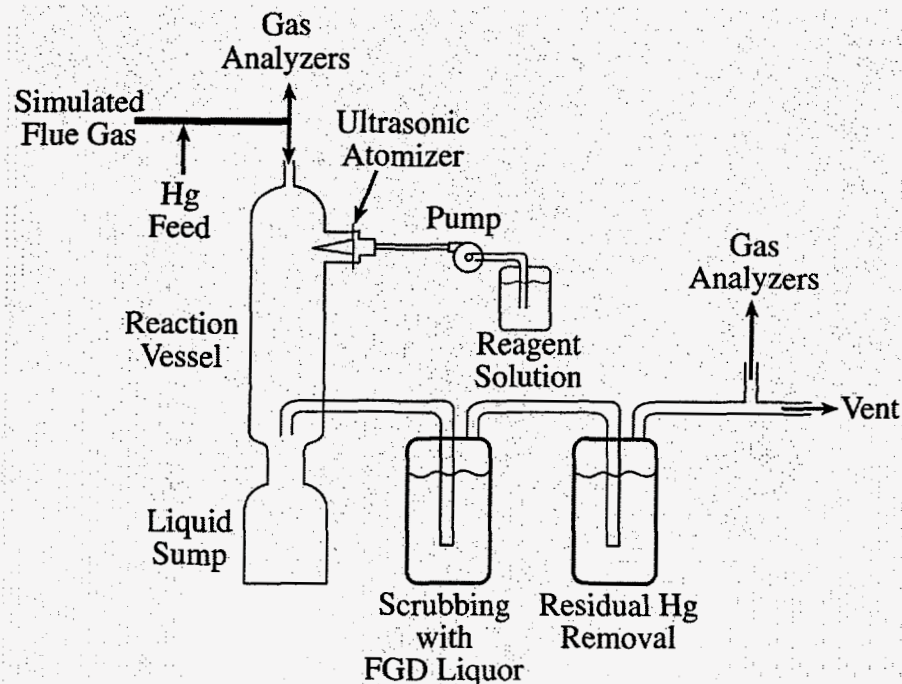


Figure 1. Diagram of Experimental Apparatus

The test duration was typically 15 min. Following each test, liquid samples were saved from the sump and the bubbler for total mercury analysis. 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 $\pm 10\%$ or $\pm 0.02 \mu\text{g/L}$, whichever is greater.

Results

NOXSORB™ Solutions

Using the concentrated NOXSORB™ solution (which contains about 18% chloric acid and 22% sodium chlorate) as the stock solution, five different solution strengths were prepared for testing. These diluted solutions ranged from 1% to 40% of the concentrated solution. The majority of the tests performed using NOXSORB™ solutions were done for gas mixtures containing nitric oxide. Results for the total amount of mercury recovered in the sump and the bubbler for these tests are given in Table 1.

For the 4% NOXSORB™ solution, tests were also performed for three different gas mixtures consisting of nitrogen plus Hg^0 , nitrogen plus Hg^0 plus carbon dioxide plus nitric oxide, and nitrogen plus Hg^0 plus carbon dioxide plus nitric oxide plus sulfur dioxide. The Hg^0 removals for these three tests were 12%, 29%, and 32%, respectively. These results show that the Hg^0

removal performance is significantly enhanced by the presence of nitric oxide (which agrees with results obtained in our earlier bubbler tests). Also, sulfur dioxide appears not to degrade Hg⁰ removal (which is quite different from the degradation of removal seen in the bubbler tests).

An additional property of NOXSORB™ solutions is its ability to remove nitric oxide. Therefore, we also measured the amounts of nitric oxide removed in those tests where nitric oxide was a component of the feed gas stream. Those results are also given in Table 1. For solution strengths of 10% and greater, removals exceeding 25% were obtained.

If the mercury removals shown in Table 1 are converted to transfer units using the formula

$$NTU = -\ln(1 - \% \text{ removal}/100),$$

the graph shown in Figure 2 is obtained. (In order to obtain a finite number for NTU, a 99% removal was assumed for the 40% NOXSORB™ case.) The linear relationship shows that Hg removal is first order in NOXSORB™ concentration. This relationship can also be a useful engineering guide for estimating the Hg⁰ removal for any given NOXSORB™ solution concentration.

Table 1. Hg and NO removals with NOXSORB™

Atomizer Solution	Hg Recovered in Liquid Phase (%)	NO Removal (%)
1% NOXSORB™	9	---*
4% NOXSORB™	29	6
10% NOXSORB™	70	25
20% NOXSORB™	90	61
40% NOXSORB™	~100	83

* A stable value for the NO in the effluent stream was not obtained for this test.

Chlorine Solutions

Four tests were performed with diluted solutions of commercially available sodium hypochlorite (containing 5% chlorine). Three tests were performed with a solution containing 1000 ppm chlorine for feed-gas mixtures containing nitrogen plus Hg⁰ plus carbon dioxide, nitrogen plus Hg⁰ plus carbon dioxide plus nitric oxide, and nitrogen plus Hg⁰ plus carbon dioxide plus nitric oxide plus sulfur dioxide. The Hg⁰ removal results for these three tests were 69%, 68%, and 14.6%, respectively. The only other test of a chlorine solution used a chlorine concentration of 5000 ppm and a feed gas mixture of nitrogen plus Hg⁰ plus carbon dioxide plus nitric oxide plus sulfur dioxide. The Hg⁰ removal for this test was 79%. These results show that very little change in Hg⁰ removal was observed when nitric oxide was added to the feed gas mixture. However, a large decrease in

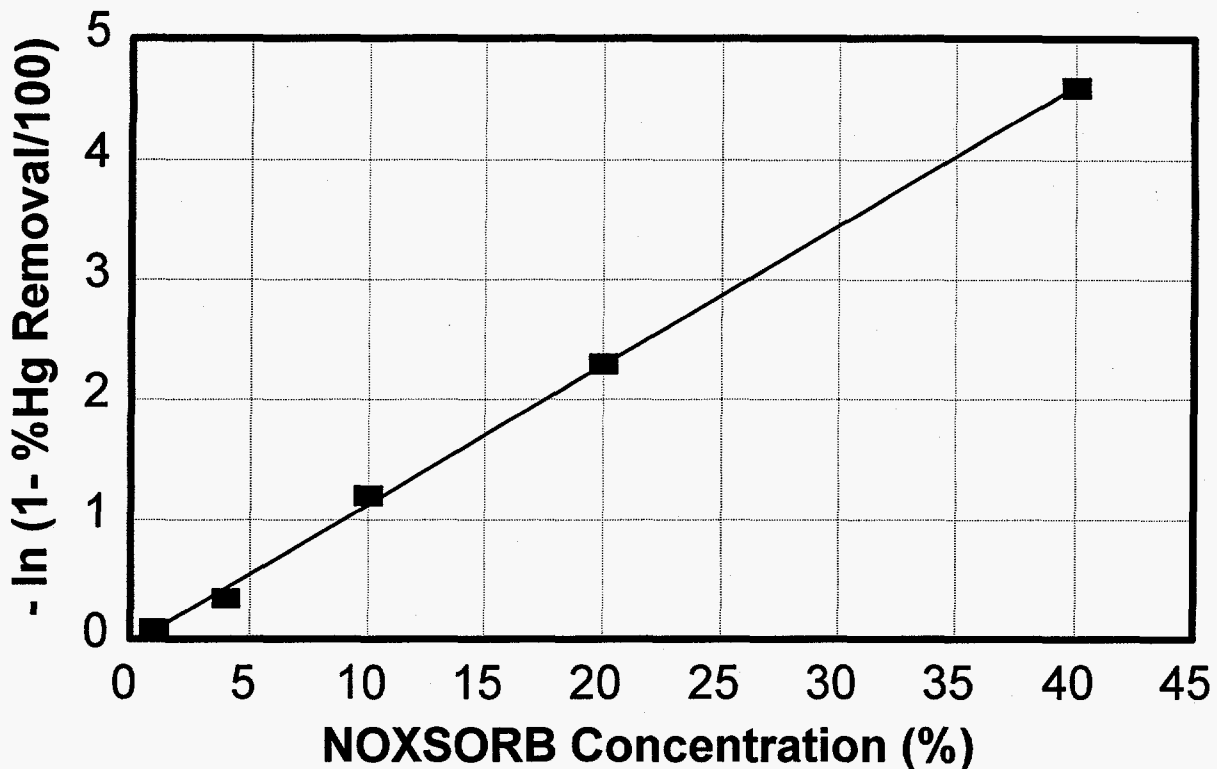


Figure 2. Mercury Removal in NTU versus NOXSORB™ Concentration

Hg⁰ removal was observed when sulfur dioxide was added to the feed-gas mixture. This decrease could be overcome by using a higher concentration of chlorine, as the result with a 5000 ppm solution demonstrates. (This result is in agreement with those obtained in the earlier bubbler tests.) The nitric oxide removal was very low and difficult to measure accurately, but it appeared to be about 10% for the three tests in which the feed-gas mixture contained nitric oxide.

Conclusions and Future Directions

The initial tests involving the atomization of chlorine or chloric-acid solutions into a flowing stream of simulated flue gas has confirmed the potential for enhanced Hg⁰ removal that was identified in the earlier bubbler and scrubber tests. At the highest NOXSORB™ concentration studied, approximately 100% of the gaseous Hg⁰ was transferred to the liquid phase. Addition of nitric oxide appeared to significantly enhance Hg⁰ removal and simultaneous removal of nitric oxide (up to about 80%) was also observed. The presence of sulfur dioxide in the flue gas did not have a negative effect on Hg⁰ and nitric oxide removals with NOXSORB™.

For chlorine solutions, up to about 75% of the Hg^0 was transferred to the liquid phase. However, nitric oxide had very little effect on Hg^0 removal and there was no significant nitric oxide removal. Addition of sulfur dioxide appeared to have a large negative effect on Hg^0 removal for chlorine solutions, although the effect could be overcome by the use of higher chlorine concentrations. While chlorine did not perform as well as NOXSORB™ under the conditions studied, process economics may be favorably influenced by the considerably lower cost of chlorine.

All of the research conducted thus far has been at room temperature. The experimental system was recently modified to provide for heating of both the feed gas and the duct so that future experiments can be conducted at temperatures comparable to those found in utility systems. We expect that the higher temperatures will improve the removal performance of the system due to better utilization of the chemical additives. This improvement should result from both better reaction kinetics at the higher temperatures and greater transfer of the reactive oxidizing species to the gas phase.

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