

## PROCESS FOR COMBINED CONTROL OF MERCURY AND NITRIC OXIDE

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## PROCESS FOR COMBINED CONTROL OF MERCURY AND NITRIC OXIDE

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### Abstract

Continuing concern about the effects of mercury in the environment may lead to requirements for the control of mercury emissions from coal-fired power plants. If such controls are mandated, the use of existing flue-gas cleanup systems, such as wet scrubbers currently employed for flue-gas desulfurization, would be desirable. Such scrubbers have been shown to be effective for capturing oxidized forms of mercury, but cannot capture the very insoluble elemental mercury ( $\text{Hg}^0$ ) that can form a significant fraction of the total emissions. At Argonne National Laboratory, we have proposed and tested a concept for enhancing removal of  $\text{Hg}^0$ , as well as nitric oxide, through introduction of an oxidizing agent into the flue gas upstream of a scrubber, which readily absorbs the soluble reaction products. Recently, we developed a new method for introducing the oxidizing agent into the flue-gas stream that dramatically improved reactant utilization. The oxidizing agent employed was NOXSORB™, which is a commercial product containing chloric acid and sodium chlorate. When a dilute solution of this agent was introduced into a gas stream containing  $\text{Hg}^0$  and other typical flue-gas species at 300°F, we found that about 100% of the mercury was removed from the gas phase and recovered in process liquids. At the same time, approximately 80% of the nitric oxide was removed. The effect of sulfur dioxide on this process was also investigated and the results showed that it slightly decreased the amount of  $\text{Hg}^0$  oxidized while appearing to increase the removal of nitric oxide from the gas phase. We are currently testing the effects of variations in NOXSORB™ concentration, sulfur dioxide concentration, nitric oxide concentration, and reaction time (residence time). Preliminary economic projections based on the results to date indicate that the chemical cost for nitric oxide oxidation could be less than \$5,000/ton removed, while for  $\text{Hg}^0$  oxidation it would be about \$20,000/lb removed.

### Introduction

Mercury was just one of many elements and compounds identified as hazardous air pollutants in Title III of the 1990 Clean Air Act Amendments. However, it has assumed singular importance for the electric utility industry. After studying the sources of mercury in the environment, the U.S. Environmental Protection Agency concluded that coal-fired boilers generate a significant fraction (on the order of 1/3) of the total anthropogenic emissions in the U.S. Those utility sources are widely dispersed and seem extremely dilute by typical air-pollution standards. However, mercury can have a lifetime of many months or even years in the atmosphere and is thus subject to long-range transport, which makes mercury control a national and international

issue. Once deposited in the terrestrial/aquatic environment, the mercury concentration in organisms can be magnified many times through the process of bioaccumulation until it becomes a potent neurotoxin for organisms near the top of the food chain (including man). The frequency of "fish advisories" warning against consumption of fish caught in certain water bodies has been increasing and there is considerable pressure to regulate all sources of mercury emissions. Coal-fired utility plants represent one of the few remaining unregulated sources.

However, recent estimates of utility control costs for mercury using duct injection of activated carbon gave values ranging from about \$25,000/lb - \$70,000/lb of mercury removed.<sup>1</sup> These costs can be contrasted with those for nitrogen oxides control, which tend to be less than \$5000/ton of pollutant removed (and that is usually considered expensive). With these high costs for "add-on" controls, techniques that utilize existing flue-gas cleaning systems for mercury removal would be desirable from both an economic and operational perspective. Particulate-matter collectors have not been shown to be very effective at capturing mercury, but some wet scrubbers installed for flue-gas desulfurization (FGD) have yielded high removals. However, the performances obtained with different scrubber systems have been highly variable with values that have ranged from about 10% to over 80%.<sup>2</sup> Determination of the factors behind these variations continues to be the subject of research.

In general, the fate of trace elements liberated in the combustion process is influenced by the type of boiler, the operating conditions, other species present in the flue gas, and the type of flue-gas cleanup (FGC) system. Mercury is a particular problem because it belongs to a group of elements and compounds denoted as Class III, which remains primarily in the vapor phase within the boiler and subsequent FGC system. It can also exist as several chemical species. In particular, the 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.<sup>3</sup> While other species are also possible and may be present in small amounts,  $Hg^0$  and mercuric chloride (see Table 1 for a list of selected chemical formulas) appear to be the most significant species for control considerations. The much greater solubility of mercuric chloride relative to  $Hg^0$  is particularly important in wet scrubbing applications. Argonne has been investigating measures for enhancing gaseous  $Hg^0$  removal in wet scrubber systems by altering the chemical form of the mercury to a water-soluble oxidized species. This paper summarizes earlier work that established the basis for the current research program and gives recent results from that program.

## Background

Argonne's research on mercury control has focused on improving the capture of  $Hg^0$  by both dry sorbents<sup>3</sup> and wet scrubbing. The initial scrubbing experiments<sup>4</sup> used a laboratory-scale scrubber that had been well characterized in previous work on combined sulfur dioxide/nitrogen oxides control.<sup>5</sup> The feed-gas stream consisted of nitrogen containing about  $40 \mu\text{g}/\text{m}^3$  of  $Hg^0$ . 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. More promising results were found when stainless steel packing was 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 high  $\text{Hg}^0$  removals and indicated that gas-phase reactions were significant in the removal process. 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.

Promising results obtained with chlorine and the apparent significance of coal-chloride concentrations for mercury capture led to further tests with a strongly oxidizing chloric-acid solution marketed by Olin Corporation under the name NOXSORB™. The scrubber was operated as a flooded column and 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  $\text{Hg}^0$ . For a batch test with a dilute (4%) solution of the as-received NOXSORB™ concentrate, an outlet reading of zero was obtained for  $\text{Hg}^0$  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

Table 1. List of Selected Chemical Formulas

Chemical Name	Chemical Formula
Bromine	$\text{Br}_2$
Carbon Dioxide	$\text{CO}_2$
Calcium Hydroxide	$\text{Ca}(\text{OH})_2$
Chloric Acid	$\text{HClO}_3$
Chlorine	$\text{Cl}_2$
Chlorous Acid	$\text{HClO}_2$
Hypochlorous Acid	$\text{HOCl}$
Iodine	$\text{I}_2$
Mercury (elemental)	$\text{Hg}^0$
Mercuric Chloride	$\text{HgCl}_2$
Nitric Oxide	$\text{NO}$
Nitrogen	$\text{N}_2$
Nitrogen Oxides	$\text{NO}_x$
Nitrosyl Chloride	$\text{NOCl}$
Oxygen	$\text{O}_2$
Sodium Chlorate	$\text{NaClO}_3$
Sulfur Dioxide	$\text{SO}_2$

to the inlet value. The breakthrough in the outlet  $\text{Hg}^0$  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 suggested nitric oxide was not solely responsible for  $\text{Hg}^0$  removal by NOXSORB™, but it seemed to promote additional reactions that enhanced the capture of mercury. 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 between  $\text{Hg}^0$ , the oxidizing additives, and the various flue-gas species, a series of experiments using bubblers was designed.<sup>6</sup> 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  $\text{Hg}^0$  conversion was determined by comparing the amount of mercury found in the bubbler solutions with the total amount of  $\text{Hg}^0$  fed in the flue gas. The  $\text{Hg}^0$  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.

Results from the bubbler tests indicated that iodine solutions could be effective in oxidizing  $\text{Hg}^0$ , even at very low iodine concentrations ( $< 1$  ppm). However, that effectiveness was lost when species other than nitrogen and  $\text{Hg}^0$  (e.g., sulfur dioxide) were in the gas stream. For bromine, substantial conversion of  $\text{Hg}^0$  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. Mercury removal with 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  $\text{Hg}^0$  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  $\text{Hg}^0$ . On the other hand, sulfur dioxide depressed the  $\text{Hg}^0$  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, which indicated that mercury could be removed if sufficient reagent was present in the flue gas.

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*  $\text{Hg}^0$  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  $\text{Hg}^0$  removal somewhat, but it remained intermediate to that with and without nitric oxide.

Additional tests that utilized different degrees of gas-liquid contacting in the bubblers indicated 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.

The cumulative results of the scrubber and bubbler studies indicated that even higher  $\text{Hg}^0$  removals might be obtained if more of the reagent was made available for reactions 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 the bubbler scenario was effectively reversed by using an ultrasonic atomizer to inject small droplets of the oxidizing solutions into a flowing gas stream containing  $\text{Hg}^0$  vapors and other typical flue-gas components. The results of those tests are described in the remainder of this paper. In addition, results are given for another method of introducing the reagent into the gas stream. This proprietary technique was recently developed and has proven extremely effective. It is currently the subject of extensive testing.

### 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. Some of the later tests also used a shorter reaction zone designed to reduce the gas residence time by a factor of about two or more. 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.

The source of  $\text{Hg}^0$  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  $\text{Hg}^0$  concentration in the gas was about  $48 \mu\text{g}/\text{m}^3$ . Bottled, high-purity (99.998%) nitrogen gas flowed around the permeation tube to produce a gas stream with a constant concentration of  $\text{Hg}^0$ . 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<sub>x</sub> 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. The gas temperature was varied between room temperature and about 350°F.

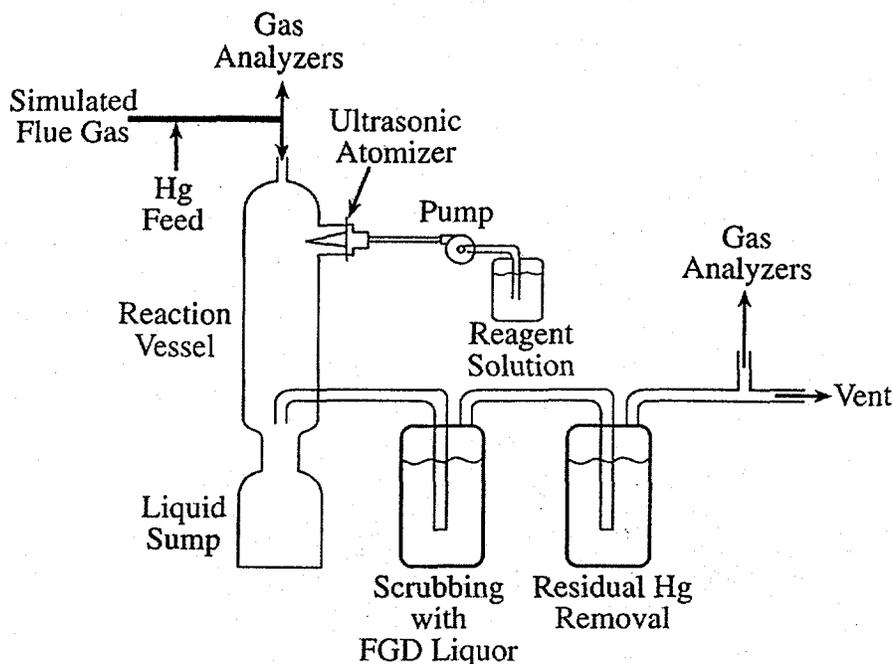


Figure 1. Diagram of Experimental Apparatus

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  $\text{Hg}^0$  and about 6 LPM for the other tests. 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.

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 - Room Temperature Ultrasonic Atomizer Injection**

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 2.

For the 4% NOXSORB™ solution, tests were also performed for three different gas mixtures consisting of nitrogen plus Hg<sup>0</sup>, nitrogen plus Hg<sup>0</sup> plus carbon dioxide plus nitric oxide, and nitrogen plus Hg<sup>0</sup> plus carbon dioxide plus nitric oxide plus sulfur dioxide. The Hg<sup>0</sup> removals for these three tests were 12%, 29%, and 32%, respectively. These results show that the Hg<sup>0</sup> 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 Hg<sup>0</sup> 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 2. For solution strengths of 10% and greater, removals exceeding 25% were obtained.

If the mercury removals shown in Table 2 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<sup>0</sup> removal is first order in NOXSORB™ concentration. This relationship can also be a useful engineering guide for estimating the Hg<sup>0</sup> removal for any given NOXSORB™ solution concentration.

Table 2. Hg<sup>0</sup> and nitric oxide 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.

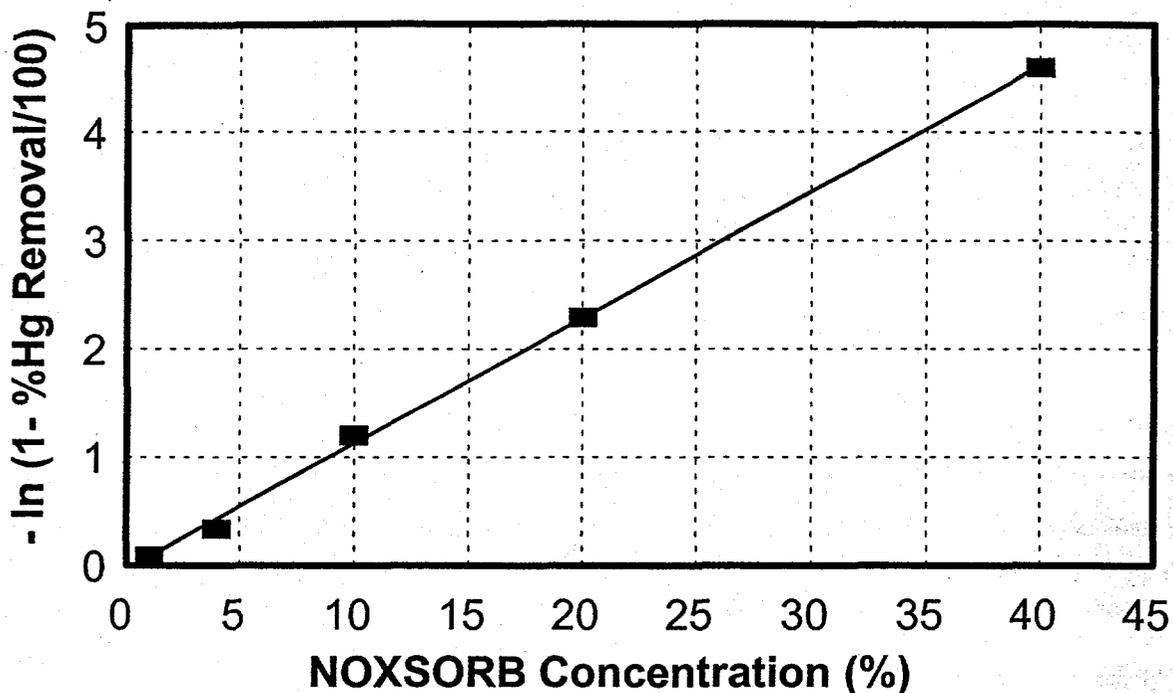


Figure 2. Mercury Removal in NTU versus NOXSORB™ Concentration

**NOXSORB™ Solutions - Elevated Temperature Ultrasonic Atomizer Injection**

A few tests were performed using the ultrasonic atomizer where the inlet gas stream and the reaction chamber were heated to between 300 - 350°F. The residence time for these tests was about 6 sec and the L/G varied from about 4 to 18. Only a limited number of tests were performed, which are summarized in Table 3 for three different combinations of variables. By comparing the results in Table 3 with those for a similar NOXSORB™ concentration in Table 2, one can see an approximate four- to six-fold increase in the Hg<sup>0</sup> removal performance in the elevated temperature tests as compared to the room temperature tests. Up to a ten-fold increase was observed in nitric oxide removal performance for the 4% NOXSORB™ solution. The nitric oxide removal performance for the 1% NOXSORB™ room temperature test was too small to be

Table 3. Hg and nitric oxide removals using an elevated reaction temperature

Atomizer Solution	Reaction Zone Temperature (°F)	Hg Recovered in Liquid Phase (%)	NO Removal (%)
1% NOXSORB™	300 <sup>a</sup>	60	30
1% NOXSORB™	350 <sup>b</sup>	56	8
4% NOXSORB™	300	96	40-60

<sup>a</sup> for this test L/G = 18; <sup>b</sup> for this test L/G = 4.

measured reliably, but it is clear that removals were also greatly increased in the elevated temperature tests.

### **NOXSORB™ Solutions - Elevated Temperature New Injection Method**

Because of the tremendous improvements in both Hg<sup>0</sup> and nitric oxide removals that were observed in the elevated temperature tests relative to the room temperature tests, we decided to perform additional elevated temperature tests using a new method for dispersing the oxidizing solution in the flue-gas stream. Because of patent considerations, we cannot yet discuss this new method in detail. To date, more than 25 tests have been performed using this method and the results obtained thus far are summarized in Tables 4 and 5.

Two important trends observed were the lower Hg<sup>0</sup> removals and the lower nitric oxide oxidation rates found with lower NOXSORB™ concentrations. These trends are illustrated in the Table 4. The residence time for these tests was about 9.5 sec, while the temperature in the reaction zone was about 280°F (140°C).

Table 4. Hg<sup>0</sup> and nitric oxide removals using a new injection method

Injected Solution	Hg Recovered in Liquid Phase (%)	NO Oxidation Rate (mL/min)
0.5% NOXSORB™	87	1.7-2.0
0.2% NOXSORB™	57	1.0-1.1
0.1% NOXSORB™	20	0.7*

\* the reliability of this result is questionable

As can be seen in Table 4, the decline in the Hg<sup>0</sup> removal with lower NOXSORB™ concentrations appears to be greater than the decline in the nitric oxide oxidation rate. Therefore, the optimum NOXSORB™ concentration (which will be critical in determining the economic operating cost) for a given process may involve tradeoffs between the Hg<sup>0</sup> and nitric oxide removals that are required.

Finally, several tests were performed using different residence times that ranged from 2 to 9.5 sec. In this case, the Hg<sup>0</sup> removal was found to decrease significantly with lower residence

Table 5. Hg<sup>0</sup> and nitric oxide removals at different residence times

Injected Solution	Residence Time (sec)	Hg Recovered in Liquid Phase (%)	NO Oxidation Rate (mL/min)
0.5% NOXSORB™	9.5	87	1.7-2.0
0.5% NOXSORB™	4	58	1.7-1.9
0.5% NOXSORB™	2	35	2.7-2.8

times, while nitric oxide removal was either steady or higher at lower residence times. The results showing these trends are given in Table 5. The reason for the higher nitric oxide oxidation rate with a residence time of 2 sec is not clear. However, a possible explanation is that a higher gas flow rate was used in this test and this may have caused better heat transfer resulting in a higher effective temperature in the reaction zone.

Recent work has focused on identifying reaction products and measuring the amount of nitrite and nitrate ions captured in the downstream bubbler solutions. Preliminary results show that we are able to capture about 70% of the oxidized nitric oxide products in our downstream bubblers. However, the results also show that besides nitrogen dioxide, other nitrogen species are likely to be produced by this oxidation method. Currently, we are performing tests to improve the capture of these products.

The reagent cost can be estimated from tests performed to date. The most efficient reagent utilization for  $\text{Hg}^0$  removal appeared to occur at a NOXSORB™ concentration of 0.2%. For this test, 2.0  $\mu\text{g}$  of  $\text{Hg}^0$  were removed in a 15 min test. The amount of NOXSORB™ solution used in that test corresponds to about 0.05 mL of the concentrate. Using a density of 1.3 g/mL and a cost of \$.70 per pound of NOXSORB™ solution, the cost for  $\text{Hg}^0$  removal is about \$22,750/lb  $\text{Hg}^0$  removed. High nitric oxide oxidation rates were obtained in several tests for various NOXSORB™ concentrations. However, the highest utilization obtained was also obtained for a test with a 0.2% solution. For this test, the nitric oxide oxidation rate varied from 1.2 to 1.3 mL/min, while the solution injection rate was about 1.9 mL/min. For a 0.2% solution, this rate corresponds to about 0.0038 mL of concentrate per min. Using these numbers, we find the cost to oxidize nitric oxide to be from about \$4,050 to \$4,300/ton. Because the manufacturer of NOXSORB™ (Olin Corporation) has told us that if their technology for producing these solutions were set up on site, the cost of NOXSORB™ solutions might be reduced by as much as 50%, the ultimate reagent cost for this method of oxidizing nitric oxide might be as low as \$2,000/ton. Additional costs would be incurred for solution handling and injection equipment, but these are expected to be relatively minor compared to the reagent cost.

### ***Chlorine Solutions - Room Temperature Ultrasonic Injection***

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  $\text{Hg}^0$  plus carbon dioxide, nitrogen plus  $\text{Hg}^0$  plus carbon dioxide plus nitric oxide, and nitrogen plus  $\text{Hg}^0$  plus carbon dioxide plus nitric oxide plus sulfur dioxide. The  $\text{Hg}^0$  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  $\text{Hg}^0$  plus carbon dioxide plus nitric oxide plus sulfur dioxide. The  $\text{Hg}^0$  removal for this test was 79%. These results show that very little change in  $\text{Hg}^0$  removal was observed when nitric oxide was added to the feed gas mixture. However, a large decrease in  $\text{Hg}^0$  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 confirmed the potential for enhanced  $\text{Hg}^0$  removal that was identified in the earlier bubbler and scrubber tests. At the highest NOXSORB™ concentration studied, approximately 100% of the gaseous  $\text{Hg}^0$  was transferred to the liquid phase. Addition of nitric oxide appeared to significantly enhance  $\text{Hg}^0$  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  $\text{Hg}^0$  and nitric oxide removals with NOXSORB™.

The use of elevated temperatures (typical of flue-gas temperatures downstream of an air preheater) significantly improved the removal of both  $\text{Hg}^0$  and nitric oxide. Both  $\text{Hg}^0$  and nitric oxide removals were found to depend upon the NOXSORB™ concentration with the new injection method. The  $\text{Hg}^0$  removal was found to depend strongly on residence time while nitric oxide removal was relatively insensitive to residence time within the range studied.

Estimates for reagent costs presented here should be viewed as extremely preliminary. However, they appear to be well within the ranges established by other control technologies for mercury and nitric oxide. Furthermore, this approach offers the possibility of a combined process that could be integrated into a wet scrubbing system for enhanced mercury removal and moderate degrees of nitric oxide control.

For chlorine solutions, up to about 75% of the  $\text{Hg}^0$  was transferred to the liquid phase. However, nitric oxide had very little effect on  $\text{Hg}^0$  removal and there was no significant nitric oxide removal. Addition of sulfur dioxide appeared to have a large negative effect on  $\text{Hg}^0$  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.

Continuing work at Argonne is currently focused on experiments that will refine our estimates of reagent requirements for combined  $\text{Hg}^0$  and nitric oxide removal. In addition, we will be attempting to identify the key reaction pathways and products in order to improve the process concept definition and evaluate any potential secondary effects.

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