Novel Economical Hg(0) Oxidation Reagent for Mercury Emissions Control from Coal-fired Boilers

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Abstract

The authors have developed a novel economical oxidant for elemental mercury (Hg(0)) removal from coal-fired boilers. The oxidation reagent was rigorously tested in a lab-scale fixed-bed column with the Norit America's FGD activated carbon (DOE's benchmark sorbent) in a typical PRB subbituminous/lignite simulated flue gas (500 ppmv SO_2, 200 ppmv NO, 10 ppbv Hg(0), 7% H_2O, 3% O_2, 12% CO_2 balanced with N_2) at 140 °C for sorbent injection. The test results showed excellent performance on Hg(0) removal by the mixture of the additive and the activated carbon. Fixed-bed results also showed that a very small amount (~10%) of activated carbon injection could eliminate almost all of the mercury generated by reaction(s) of Hg(0) with the additive, indicating promising use in subbituminous/lignite flue gases with relatively high Hg(0) content.

A preliminary cost estimate for sorbent injection was almost 70~80% less than that of raw FGD activated carbon at subbituminous and lignite-firing sites. The additive is thermally stable up to 350 °C, suggesting potential high-temperature applications for coal gasification and hot-side electrostatic precipitator. As an alternative, the oxidized mercury generated from reaction(s) with the additive could be removed in wet scrubbers due to its high solubility in water. Therefore, the additive can be applied to virtually all coal-fired power plants where Hg(0) emissions are relatively high such as PRB subbituminous and/or lignite coal-firing sites as an economical and viable option.

Introduction

According to U.S. EPA analyses[1], recent estimates of annual total global mercury emissions from natural and anthropogenic sources range from approximately 4,400 to 7,500 tons per year. Anthropogenic U.S. mercury emissions are estimated to account for approximately 3% of the total global emissions, and coal-fired power plants in the U.S. are estimated to contribute to approximately 1% of the total global mercury emissions, which accounts for 33% of anthropogenic U.S. emissions. An additional EPA study concludes that regional transport of mercury emission from coal-fired boilers in the U.S. is responsible for its contribution to U.S. waters. Three forms of mercury are released from coal-fired boilers: elemental mercury (Hg(0)), oxidized mercury (Hg(+) or Hg(2+)), and particulate mercury. Among these forms, elemental mercury can be transported thousands of miles before depositing to land and water. On March 15, 2005, U.S. EPA announced the Clean Air Mercury

Rule[2] to permanently limit mercury emissions from coal-fired power plants. The first-phase cap is 38 tons beginning in 2010, with a final cap set at 15 tons starting in 2018, resulting in nearly 70% reductions of 1999 emission levels.

Sorbent injection is one of the most promising family of technologies applicable to the utility industry as virtually all coal-fired boilers are equipped with either an electrostatic precipitator (ESP) or a baghouse. Among various sorbents tested through the Department of Energy (DOE)'s field testing program, the most widely tested and promising sorbent is raw activated carbon, and it demonstrated the capability of capturing both of elemental and oxidized mercury from flue gas streams. However, the activated carbon still has the following problems: (1) raw activated carbon is still expensive (e.g., Norit DARCO FGD activated carbon, DOE's benchmark sorbent, costs $0.42/lb); (2) it requires a very high carbon-to-mercury mass ratio (3,000~100,000)[1] especially in flue gases with low HCl content such as subbituminous and lignite coal; (3) it also turned out to degrade the quality of fly ash and give an adverse impact on its sales as pozzolan additive.[3] Therefore, there are strong needs for developing efficient and cost-effective noncarbon-based sorbents.

The primary objective of this study is to develop and test advanced noncarbonaceous solid sorbent materials suitable for removing mercury in the elemental form from power plant emissions, preferably as a discrete waste to minimize formation of toxic waste generation. An efficient and cost-effective novel Hg(0) oxidant was evaluated in a lab-scale fixed-bed system, and its results are presented in this article.

EXPERIMENTATION

General Procedure

An elemental mercury permeation tube (VICI Metronics, Inc) was used to steadily inject Hg(0) vapor into the system. A flow rate of 100 mL/min of N_2 carrier gas (>99.998%) passed over the permeation tube immersed in a temperature-controlled water bath to sweep Hg(0) released from the permeation device, and was maintained at all times with a mass flow controller (MFC). The 3-cm long permeation tube immersed in a water bath was set to release Hg(0) vapor at a rate of 78 ng/min, which gives steady 85 μg/Nm^3 of an inlet Hg(0) concentration for this experiment. The water bath was operated at 55.5 °C within ±0.2 °C to meet the specified inlet Hg(0) concentration. The influent Hg(0) vapor concentration was repeatedly measured with 4% (w/v) $KMnO_4$/10% (v/v) H_2SO_4 impinger solutions, and was confirmed that the variations were within ±0.5 ppbv.

A blank test was carried out prior to the main experimental study on mercury uptake by sorbents in order to examine the adsorption of mercury vapor on tubing, reactor, and blank glass fiber filter. The system was cleaned with 10%(v/v) nitric acid and de-ionized water before each experiment to remove residual mercury in the system as described in the Ontario Hydro Method.[4]

Fixed-Bed System

A fixed-bed system shown in Figure 1 was used to test a set of new sorbents under a simulated flue gas condition listed in Table 1. A sorbent sample was mixed in a silica (SiO_2, Fisher Scientific, fine granules, particle size: 149–420 μm) diluent prior to being packed in the reactor. Approximately 50 mg of each sorbent in 6 g of silica was used, and the bed material was supported by a fritted quartz disk with a Teflon o-ring and a glass fiber filter with a nominal 1 μm pore diameter in order to minimize channeling and prevent the sorbent from escaping through the bed. All testing conditions are summarized in Table 2. An additional filter system with a glass fiber filter with a nominal 0.7 μm pore diameter was used at the outlet of the reactor to capture sorbent particles potentially escaping from the bed.

The fixed-bed reactor was constructed to allow for a total flow of 1 L/min gas throughput at 23 C. The inside diameter of the reactor (1.27 cm = ½”) made of borosilicate glass was selected to meet a superficial velocity of 13 cm/s at 23 °C in the empty bed reactor. The superficial velocity of the simulated flue gas was chosen to simulate a flow pattern in the ductwork of coal-fired utility plants (~50 ft/s = ~1,500 cm/s), an electrostatic precipitator (ESP) (~5 ft/s = ~152 cm/s), and a fabric filter (~3 ft/min = ~2 cm/s).

Table 1. Simulated flue gas condition

H_2O	O_2	CO_2	SO_2	NO	HCl	Hg(0)
7 %(v)	3%(v)	12%(v)	500 ppmv	200 ppmv	0 ppmv	9 ppbv

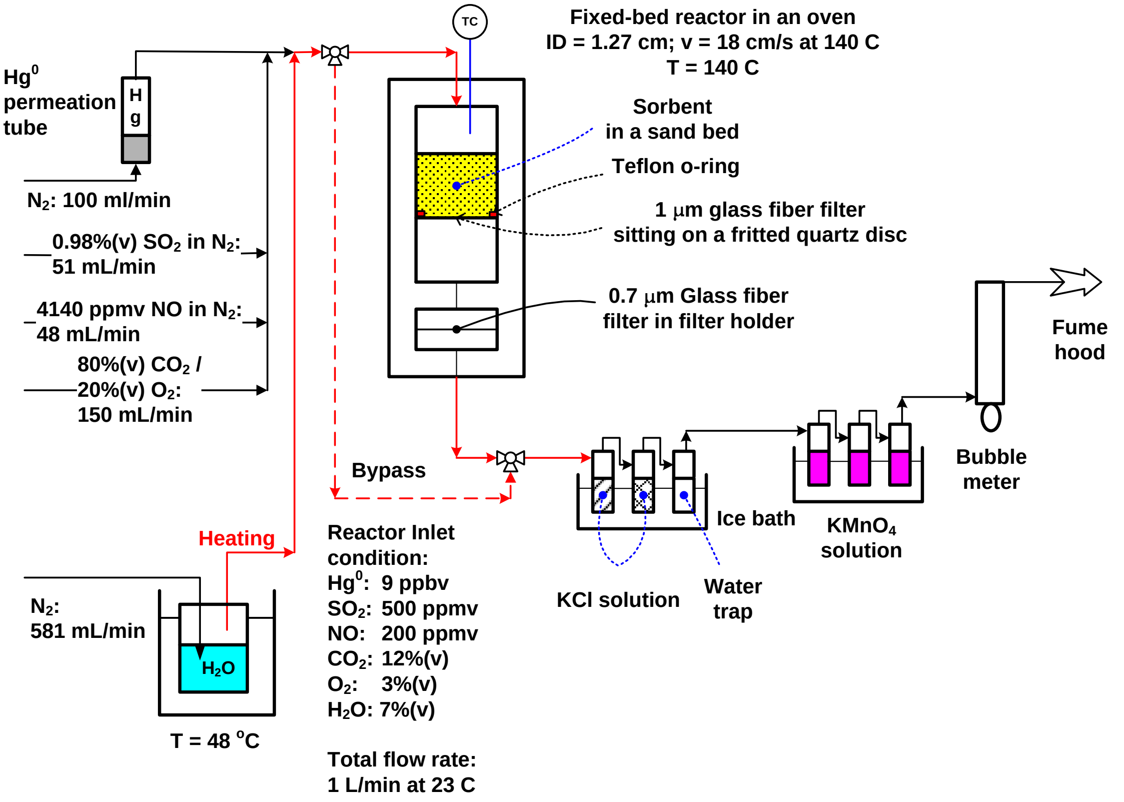

Figure 1. Schematic of a fixed-bed apparatus.

Table 2. Summary of testing conditions

Item	Testing Conditions
Reactor	½-in. (1.28 cm) i.d. borosilicate
Temperature (°C)	140
Flow rate (cm^3/min)	1,000 @ 23 °C; 1,395 @ 140 °C
Flow mode	Downflow
Superficial velocity in an empty reactor (cm/s)	13 @ 23 °C; 18 @ 140 °C
Residence time in an empty reactor (s)	0.23 @ 23 °C; 0.17 @ 140 °C
Sorbent	50 mg in 6 g of a sand bed
Gas	Simulated flue gas
Inlet Hg(0) concentration	78 ng/min = 9 ppbv = 85 $\mu g/Nm^3$
Adsorption capacity determination (1-hour testing)	Ontario Hydro Method (spent sorbent analysis and impinger solution analysis)

During each test, the mercury-laden inlet gas bypassed the sorbent bed, and passed to the analytical system until the desired inlet mercury concentration was established. Then, the adsorption test was initiated by diverting the gas flow through the sorbent column in downflow mode to minimize the potential for fluidization of the bed. All of the tubing and valves in contact with Hg(0) are constructed from Teflon, which has been demonstrated to have good chemical resistance and inertness towards elemental mercury. The sorbent bed and filter system was placed in a temperature-controllable convection oven, which maintained the system temperature within ±0.5 °C. A Teflon-coated thermocouple was installed in the fixed-bed reactor to control the gas temperature at the inlet of the sorbent bed.

When mercury speciation studies were conducted, an impinger train using the Ontario Hydro Method was placed on the outlet side of the system for obtaining speciated mercury samples. The effluent mercury vapor can be fully or partially oxidized due to reactions between elemental mercury, a sorbent, and other flue gas components. Therefore, a 1 M KCl solution was used to capture potentially oxidized mercury, and an additional water trap was used to remove condensed water vapor as shown in Figure 1. Prior to the main experiments, blank tests confirmed that the amount of mercury captured in the 1 M KCl solution and water trap was negligible. The total gas flow rate was monitored at the outlet of the impinger system using a bubble flow meter. It was confirmed that consistently reproducible results were obtained with this experimental setup.

Results and Discussion

Fixed-Bed Test Results

All of the one-hour tests were conducted at 140 °C in the fixed-bed system, and their results are summarized in Table 3. The mass balance closure for all runs was in a reasonably acceptable range (87−106%), and the amount of mercury captured in spent sorbents was determined after performing the digestion procedures described in the Ontario Hydro Method. Please note that HCl gas was not added to the simulated flue gas for all the runs listed in order to eliminate the well-known heterogeneous mercury oxidation (mercury adsorption on activated carbon after *in-situ* HCl gas impregnation on activated carbon).[5] However, the performance of the novel oxidant proved not to be affected by an addition of HCl gas from additional testing with the addition of HCl.

Run 1 showed 11% of mercury capture in the novel oxidant, and approximately 74% of the mercury emissions from the bed were captured **as oxidized mercury** in the second filter placed in a filter holder, a water condensation impinger, and KCl solution impingers. Run 1 showed that mercury adsorption in the novel oxidant was relatively small (approximately 10% of total Hg(0) injected into the system), and a significant majority of the inlet Hg(0) vapor was converted to the oxidized mercury form and adsorbed onto the solid phase (filter) or absorbed into the aqueous phase bubbler where water or KCl solution was placed. Therefore, the novel oxidant was found to be an excellent Hg(0) oxidant. In Run 2, raw Norit FGD activated carbon (DOE's benchmark sorbent) was tested in order to determine its Hg(0) adsorption capacity in the absence of HCl in the gas phase. These tests showed 26% sorption capacity and negligible oxidation capability. In our early tests, raw activated carbon did not work well for Hg(0) removal without HCl gas in any type of simulated flue gases. These results in the absence of HCl gas corroborate low mercury removal observed from the flue gases of PRB subbituminous and lignite coals in the DOE's Mercury Control Field Testing Program[3] and another fixed-bed study[5].

Runs 3 and 4 were performed to examine the possibility of capturing the oxidized mercury created from the use of the novel oxidant by the *in-situ* adsorption onto activated carbon. A stannous chloride (a reducing agent; $SnCl_2$) solution was used for Run 3 for total mercury analysis after the fixed-bed reactor so that all the mercury emitted after the bed would be converted to Hg(0), and could be collected in the downstream $KMnO_4$ solution impingers. Run 3 employed 20% (10 mg) of the FGD activated carbon after uniformly mixing it with 80% (40 mg) the novel oxidant in 6 g of sand. Its result showed that almost all Hg(0) (98% of the total 87% recovered mercury from all impinger solutions, and digestions of filters and solids) was captured in the mixture of the two materials (FGD activated carbon and novel oxidant) with 20% addition of the FGD activated carbon. In Run 4, the amount of FGD activated carbon was reduced to the half that of Run 3, 10% (5 mg), and was tested under the same conditions. The 10% addition of the activated carbon also demonstrated almost the same performance in Hg(0) removal as that of Run 3 under the same test conditions. Since the majority of the sorbent cost comes from that of the activated carbon (current Norit's FGD activated carbon's cost is $0.42/lb), it is very crucial to minimize the amount of activated carbon used.

Table 3. 1-hr testing results in a fixed-bed reactor at 140 °C

Run	Sorbent	Loading (mg sorbent in 6 g sand)	Hg from spent sorbent + filter (%)	Hg from 2^{nd} filter in filter holder (%)	Hg in water condensation (%)	Hg in tubing (%)	Hg in KCl (%)	Hg in $KMnO_4$ (%)	Mass balance closure based on inlet Hg (%)
1	A**	50	11	19	28	0	27	14	100

2	AC**	50	26	N/A	0	0	0.5	73	106
3	A+AC*	40 + 10	98	N/A	0	0	N/A	2	87
4	A+AC**	45 + 5	96	1	0	0	1	2	90

(Note)
A = Novel oxidant
AC = Norit's FGD activated carbon
* Impinger configuration for total mercury analysis: 2 $SnCl_2$ → 1 water trap → 3 $KMnO_4$
** Impinger configuration for mercury speciation analysis: 2 KCl → 1 water trap → 3 $KMnO_4$

From the above test results, the novel oxidant proved to exhibit excellent performance and selectivity in removing Hg(0). It is anticipated that injection of the novel oxidant in conjunction with raw activated carbon could achieve 90%+ mercury removal in a cost-effective way, especially for flue gases with relatively high Hg(0) content.

An adsorption capacity of each sorbent was determined using the digestion procedure described in the Ontario Hydro Method, and is shown in Figure 3. It clearly shows that the FGD activated carbon's utilization can be greatly enhanced by the addition of the novel oxidant. These results obtained from the fixed-bed tests are expected to be replicated through sorbent injection prior to a fabric filter system in a large scale system.

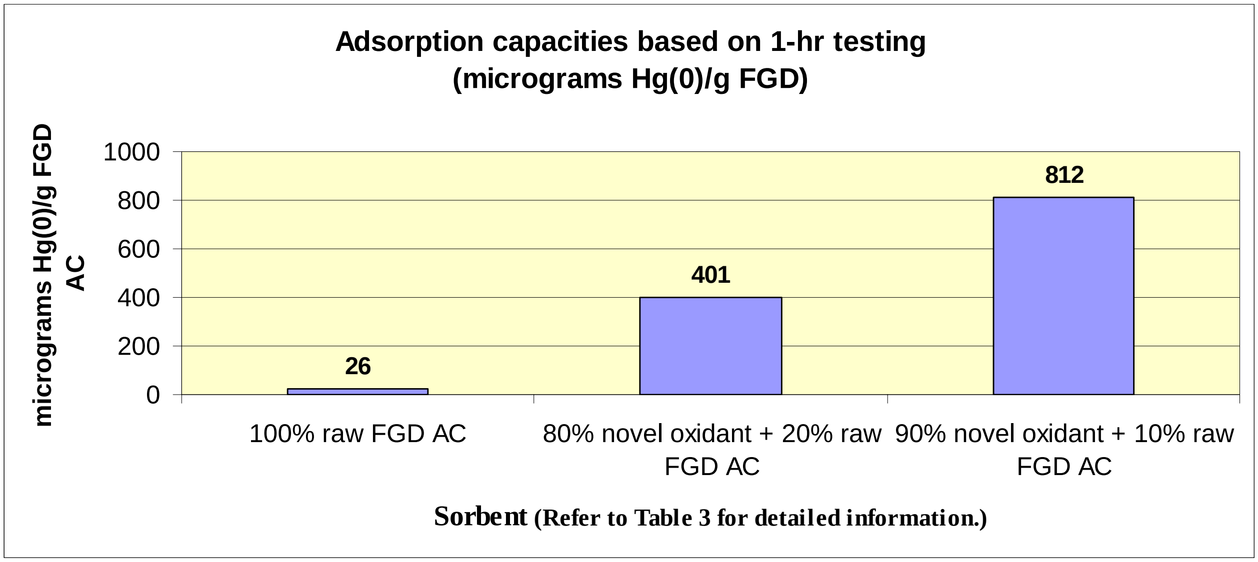

Figure 3. Adsorption capacities for three different sorbents obtained through 1-hour tests.

Cost Analysis

Based on the Hg(0) removal efficiencies as shown in Figure 3, sorbent costs were estimated as shown in Table 4. The sorbent prices were estimated based on a current price of the FGD activated carbon ($0.42/lb) and a projected price of the novel oxidant ($0.10–0.25/lb). It clearly shows that approximately 80–90% cost reductions in mercury control can be expected using the novel oxidant in conjunction with the FGD activated carbon with a dramatic increase in Hg(0) removal efficiencies from 26 to almost 100% regardless of the HCl concentration levels in the flue gas. The projected cost of sorbent injection is expected to be almost one order of magnitude lower than that of raw FGD activated carbon injection.

Table 4. Estimated sorbent costs based on 1-hr fixed-bed tests

	100% raw FGD AC	**80% novel oxidant + 20% raw FGD AC**	**90% novel oxidant + 10% raw FGD AC**
Removal efficiency (%)	26	98	98
Estimated cost of FGD AC (excluding the cost of the novel oxidant) based on 1-hr testing ($/lb Hg(0) removal)	16,153	1,049	518
Sorbent cost per lb ($/lb)*	0.42	0.16~0.28	0.13~0.27
Estimated cost of total sorbents (FGD AC + the novel oxidant) based on 1-hr testing ($/lb Hg(0) removal)	16,153	1,998~3,491	1,603~3,328

(Note) *Sorbent price was estimated based on a current price of the FGD AC ($0.42/lb) and a projected price of the novel oxidant ($0.10~0.25/lb).

Also, as an additional advantage of using this oxidant, and as an alternative for power plants with wet flue gas desulphurization systems, the oxidized mercury emitted from the reaction with the novel oxidant could be removed in wet scrubbers due to the high solubility of oxidized mercury in water (Refer to the results of Run 1 and 2 in Table 3). Therefore, the injection of the novel oxidant can be applied as an economical and viable option to virtually all coal-fired power plants where the Hg(0) emissions are relatively high, such as those stations burning Powder River Basin (PRB) subbituminous and/or lignite coal.

Conclusions

Based on the experimental results and previous studies reported in the literature, the novel oxidant is expected to have the following advantages:

1) The injection of the novel oxidant in conjunction with activated carbon can achieve 90%+ mercury removal regardless of the mercury speciation present in the flue gas. It is well known and proven through field testing that most of oxidized mercury can be readily removed using activated carbon.

2) The kinetics of the novel material appears to be fast enough to react with Hg(0) in ~0.1 s based on an empty bed contact time (~0.17 s at 140 °C). Thus, sorbent dispersion and mass transfer resistance would be a rate determining step in mercury removal. However, this needs to be verified by extensive pilot-scale testing.

3) Unlike other halogenated activated carbon sorbents, the dopant chemical is thermally very stable up to 350 °C, and undesirable flue gas halides (i.e., off-gassing of halogen) will be minimized.

4) As the novel material has been shown to have excellent oxidant capability, it can be injected in conjunction or concomitantly with activated carbon to achieve 90%+ mercury removal and collected in particulate control devices such as ESPs or fabric filters. As an alternative, only the novel cost-effective material reported here can be injected prior to a wet scrubber if it is available, and oxidized mercury can be removed in the wet scrubber. In this scenario, the sorbent/oxidant would be injected upstream of the existing ESP and captured, while the resultant highly oxidized mercury would be absorbed into the downstream wet scrubber.

5) If successful, the novel oxidant will result in a significant cost reduction in mercury control (> 50%). The use of the novel oxidant is also expected to have a negligible effect on fly ash byproduct sales and use. The compositions of the substrate material of the novel oxidant are very similar to those of fly ashes, and the injection of the material is not likely to result in an adverse impact on fly ash sales.

6) In the early stage of testing the novel material proved to have a small but measurable SO_2 removal capacity.

REFERENCES

1. *Mercury Study Report to Congress*. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC. 1997, http://www.epa.gov/mercury/report.htm.

2. *Clean Air Mercury Rule*. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC. 2005, http://www.epa.gov/air/mercuryrule/index.htm.

3. Feeley, T. J.; Brickett, L. A.; O'Palko, B. A.; Murphy, J. T. Field Testing of Mercury Control Technologies for Coal-Fired Power Plants. National Energy Technology Laboratory, U.S. Department of Energy: Pittsburgh, PA. http://www.netl.doe.gov/coal/E&WR/mercury/index.html.

4. ASTM Method D6784-02, "Standard Test Method for Elemental, Oxidized, Particle-bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)".

5. Carey, T. R.; Hargrove Jr., O. W.; Richardson, C. F.; Chang, R.; Meserole, F. B. Factors Affecting Mercury Control in Utility Flue Gas Using Activated Carbon. *J. Air & Waste Manage. Assoc*. **1998**, *48*, 1166.