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High-Temperature Sorbents to Lower Mercury Control Costs

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An inexpensive material was recently dveloped that appears to effectively capture mercury from simulated coal-fired flue gases when injected into ductwork at modest rates. Importantly, the new sorbents appear to be effective at high temperatures, 300°F to 400°F. This means that inexpensive gas-cooling or fabric-filter retrofits are not required and that fly ash will remain saleable. Consequently, preliminary estimates of their cost effectiveness suggest costs approximately one-tenth of those estimated by the EPA for other technologies.

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"High-Temperature Sorbents to Lower Mercury Control Costs"

Sid Nelson Jr.
Sorbent Technologies Corporation

Summary

An inexpensive material was recently discovered that appears to effectively capture elemental mercury from simulated coal-fired flue gases when injected into ductwork at modest rates. Importantly, the new sorbents appear to be effective at high temperatures, 300°F to 400°F. This means that expensive gas-cooling or fabric-filter retrofits are not required and that fly ash sales can remain unaffected. Consequently, preliminary estimates of their cost-effectiveness suggest costs approximately one-tenth of those estimated by the EPA for other technologies.

Background

Utility mercury emissions are a very difficult technical problem. The high gas flows and low concentrations of mercury in their flue gases make mercury technologies that work on smaller streams impractical for utility use. Moreover, power plants emit elemental mercury, Hg(0), as well as oxidized mercury, mostly expected to be $HgCl_2$. The elemental form of mercury has proven to be especially difficult to control. While there is wide variation between plants in the relative amounts of their flue-gas mercury species, many emit significant elemental mercury.

A very easy control method to retrofit is to simply inject a mercury sorbent material into the flue gas ahead of an existing electrostatic precipitator. The bulk of coal-fired power plants in the U.S. have their flue gases readily available for retrofitted treatment between their air preheaters and electrostatic precipitators, where the temperature is from about 300°F to 400°F. Powdered activated carbon (PAC) is frequently suggested as such a duct-injected sorbent. Unfortunately, however, the results of activated carbon injection tests to date at power plants have been highly variable and not particularly promising. Activated carbons generally appear to perform poorly on mercury at temperatures above about 250°F. Gas cooling by water injection is possible, but this would be expensive to operate and could cause significant downstream corrosion and opacity problems.

Sorbent Technologies Corporation has been investigating mercury removal from flue gases for over five years. During that time a multitude of compounds were examined for their mercury-removal abilities for use in gas-phase, wet-scrubbing, fixed-bed, and duct-injection processes. In pursuing this research, a new sorbent material was discovered that captures significant elemental mercury when injected into coal-fired flue-gas compositions at high 300° to 400°F temperatures. This new Sorbtech Hg sorbent appears to have the potential to significantly lower elemental mercury removal costs at coal-fired power plants.

If required to remove mercury from their flue gases, coal-fired utilities may face significant expenses. Below is a section of a table taken directly from the recent multi-volume EPA Mercury Report to Congress. The table summarizes the cost effectiveness of various combinations of existing technologies modeled by the EPA and DOE for various plant situations. Note that in the majority of situations, the cost effectiveness, as noted in the final column, range in the tens of thousands of dollars per pound of mercury removed. The reason for such high costs is primarily because expensive spray cooling and/or fabric filters are generally required to get powdered activated carbons, the best available current technology, to work at even high injection rates on most hot, ESP-equipped flue-gas streams.

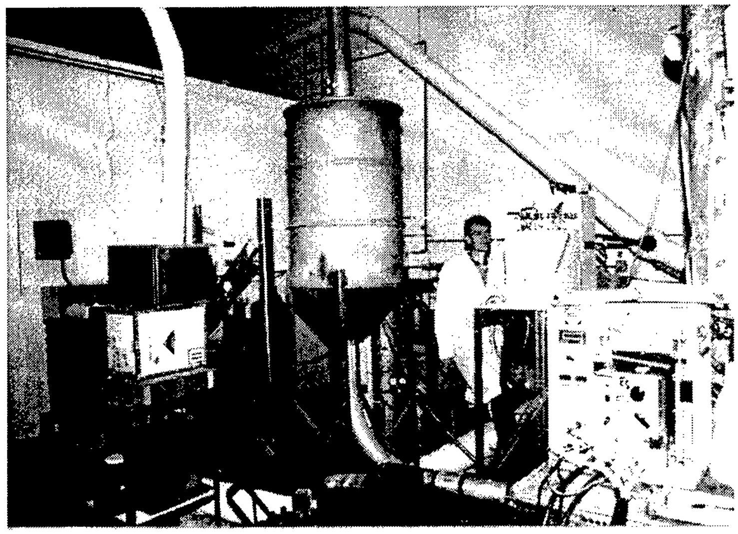
Table 3-2
Cost Effectiveness of Control Technologies for Utility Boilers

Model	Model Definition		Sensitivity Analysis for Models			
	Size (MW)	Mercury Control	Source	Carbon Usage (g C/g Hg)	Cost Effect. (mils/kWh)	Cost Effect. ($/lb Hg)
1a	975	AC injection	EPA	34,200	1.82	22,100
			DOE	100,000	5.58	67,700
1b	975	Spray cooler, AC injection, fabric filter	EPA	460	1.43	17,400
			DOE	9,400	2.10	25,400
1c	975	Spray cooler, AC injection	EPA	460	0.40	4,940
			DOE	30,000	2.19	26,500
1d	975	Carbon filter bed	EPA	--[b]	2.70	32,700
			DOE	--	NA[c]	NA
2	975	Carbon filter bed High-sulfur Coal	EPA	--	3.1	37,800
			DOE	--	NA	NA
3a	100	AC injection	EPA	17,200	1.16	14,200
			DOE	100,000	5.71	70,000
3b	100	Spray cooler, AC injection, fabric filter	EPA	460	2.09	27,700
			DOE	12,600	3.15	38,600

By performing well at the high available flue-gas temperatures, at modest injection rates, and during the brief time available in the ductwork, the new sorbents may prove much more cost-effective. The following sections describe initial duct-injection testing of the new materials.

Experimental Apparatus

Initial screening and development work was performed using laboratory-scale fixed beds. However, sorbents intended for duct-injection use require testing in an actual duct-injection apparatus. Consequently, a fully-instrumented 80-acfm duct-injection test facility is now being used at Sorbent Technologies. This facility includes a propane burner assembly; SO_2 and NOx spiking from bottled gases; an elemental mercury spiking subsystem with mercury permeation tubes; a sorbent screw feeder and fluidizing injection subsystem; 80-feet of insulated, 2.5-in. diameter pipe "ducting"; thermocouples; a 2-bag fabric filter; safety filter; orifice plate to measure flow; and variable-speed I.D. fan. Mercury sampling and analysis equipment includes multiple EPA Method 29/ Ontario Hydro six-impinger sampling trains, a heated particulate trap, heat-traced probe, dry gas meter, scalping cyclone, and Jupiter double-beam cold vapor atomic adsorption (CVAA) unit. A photograph and diagram of the system follow.



Photograph of the duct-injection test system.

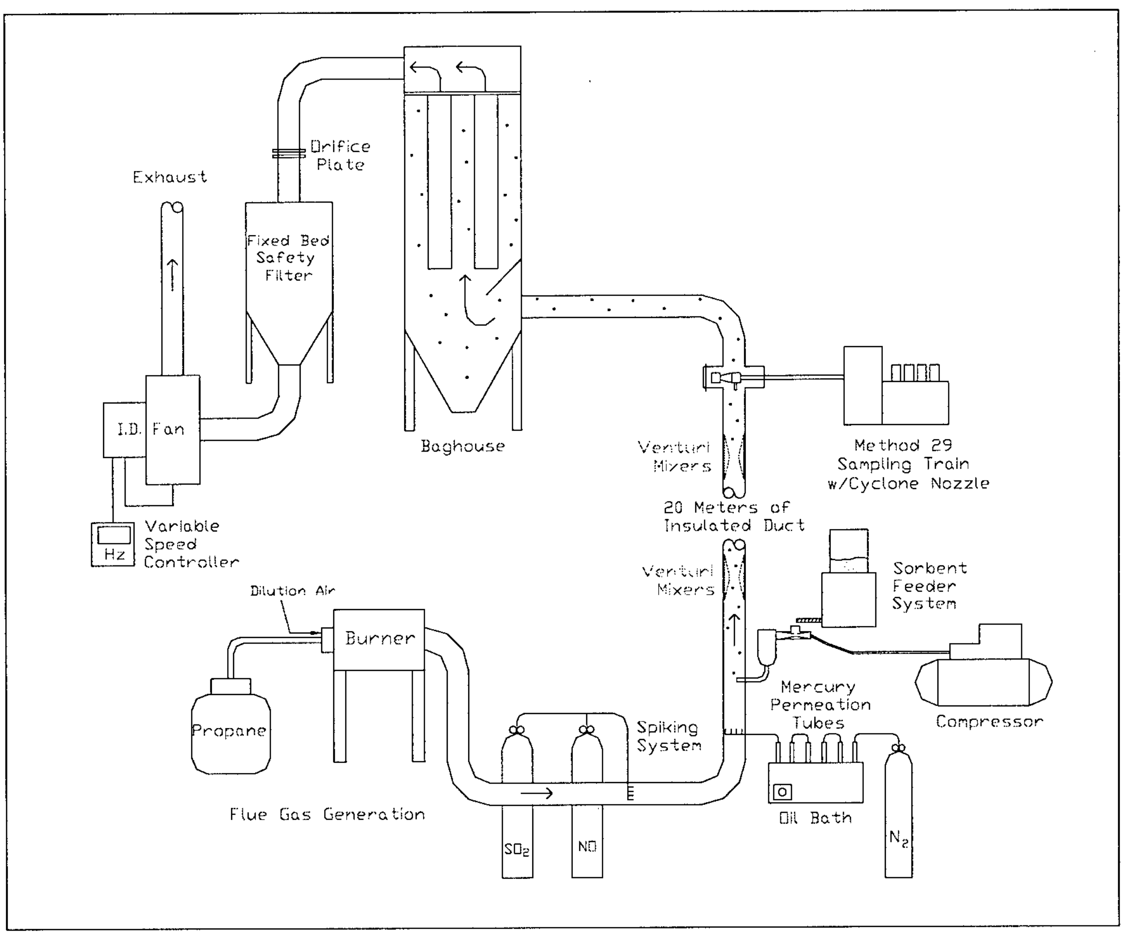


Diagram of the duct-injection test system

When sampling from a sorbent-laden gas stream, it is imperative that no sorbent particles enter the sampling train. If sorbent is deposited in the probe or on the pre-filter, it can adsorb mercury from the sampled gas, and result in erroneous measurements. Prior experiments on the duct-injection test system indicated that by adding a sampling cyclone ahead of the probe, turning the probe tip away from the gas flow (non-isokinetically), and by keeping the train pre-filter above at least 275°F, measurement interference due to particulate can be minimized. Further, as a safety check, washes of both the sampling probe and the filter assembly are always also analyzed to signal any inadvertent mercury capture and erroneous data.

Original Duct Injection Results

Following numerous shake-down runs, where various improvements were made to the duct-injection test system, Sorbtech's new Hg sorbent was tested against a standard powdered activated carbon used for air pollution control, Norit FGD®. In these runs a high-sulfur coal flue gas was simulated with hot gas from the burner spiked with acid gases from cylinders. Diffusion tubes in an oil bath added elemental mercury to approximately 30 [g/Nm^3. The 80-acfm of gas flowed at about 30 ft/sec with a residence time between the sorbent-injection and gas-sampling points of about 2 seconds. Sampling occurs before the baghouse, so that only in-flight mercury removal is measured. Once the system reaches a steady state, the ductwork loses about 50°F to the surroundings between the injection and sampling ports. The spiked NO typically converts to about 95% NO and 5% NO_2 when mixed with O_2 in the injection gas. The various test parameters follow.

Sorbent:Hg mass:	3,000:1	SO_2:	1500 ppm
Temp. @ injection:	350°F	NO:	600 ppm
Temp. @ sampling:	300°F	HCl:	60 ppm

Individual trials were then run with: 1) the commercial powdered activated carbon, Norit FGD®, and 2) the new Sorbtech Hg sorbent. The two materials were each injected into the gas stream at a mass ratio rate of about 3,000:1 of sorbent to Hg.

Gas samples were each drawn before the baghouse for one-hour periods through an EPA Method 29 sampling train, modified as per the "Ontario Hydro" mercury speciation method. A pre-sampling cyclone was used to prevent any carbon from entering the sampling train and the sampling pre-filter box was always kept above 275°F so that any collected carbon would adsorb little mercury. The collected and immediately-preserved samples from the various impingers were then processed according to the Ontario Hydro method and analyzed by CVAA for their mercury levels. Washes of both the probe and pre-filter in each run were analyzed and no significant sample-train mercury was detected. The speciated results appear below.

	$Hg^{(0)}$, µg/Nm^3	**$Hg^{(+2)}$, µg/Nm^3**	**Total Hg, µg/Nm^3**
Norit FGD®	25.0	3.3	**28.3**
Sorbtech Hg sorbent	9.3	4.0	**13.3**

Injection of the Sorbtech Hg sorbent at 350°F resulted in less than half the mercury emissions of the activated carbon.

A similar series of runs was then made simulating the combustion stream of a low-sulfur coal. The test parameters appear below:

Sorbent:Hg mass:	1,500:1	SO_2:	400 ppm
Temp. @ injection:	350°F	NO:	400 ppm
Temp. @ sampling:	300°F	HCl:	0 ppm

In these trials, the new Sorbtech Hg sorbent was tested after a baseline run without any sorbent injection. When the sorbent feeder was turned on, the materials were injected at the very low rate of 1,500:1 of sorbent to Hg on a mass basis. The prior Ontario Hydro mercury sampling and analysis procedures were repeated. The results follow.

	$Hg^{(0)}$, μg/Nm³	$Hg^{(+2)}$, μg/Nm³	Total Hg, μg/Nm³	Removal
Baseline – No injection	36.0	0.8	36.8	-
Sorbtech Hg sorbent	12.3	1.6	13.9	**62%**

In this instance, the Sorbtech Hg sorbent removed over 60% of the elemental mercury.

It is possible that these removal rates would be even higher on a full-scale gas stream because of limitations in the test equipment that was used. Because so little sorbent was being fed by the screw feeder -- only 80 mg/min, or 1.3 mg/sec -- substantial "pulsing" of the sorbent injection was noted. Consequently, some slugs of flue gas probably never saw the sorbent. This would not be the case in a larger installation. Additional mercury removal would also be expected with residence time in a fabric filter or electrostatic precipitator. However, considering the ease of application, the difficult elemental form of the mercury, and the early stage of development, these initial results are quite promising.

Merck Testing

Merck & Co., the large drug company, recently tested the new Sorbtech Hg sorbent in a bench-scale rotary-kiln-fired fixed-bed apparatus of theirs. The unit simulates their thermal desorption facility for mercury-contaminated soil near a Rahway, New Jersey plant. What follows is quoted directly from Merck's test report to Sorbent Technologies:

"Four grams of sorbent were used. The adsorbents were heated to about 400°F and the kiln gases were passed through the sorbent to capture the mercury vapors. The gas composition was 10% O_2, 3.2% CO_2, 100 ppm NOx, 11 ppm SO_2, and the balance was nitrogen. The gas flow rate was 4 L/minute and the test duration was 1 hour. Off-gases were captured in a potassium permanganate solution. At the end of each run, the treated soil, the sorbent, and the potassium permanganate solution were analyzed for total mercury and the mass balance was calculated." Their results follow:

Merck Testing Results of Sorbtech Hg Sorbent	
Mass of mercury in soil	4.4 mg
Residual mass of mercury in soil	0.1 mg
Mass of mercury in off-gas after sorbent	0.2 mg
Mass of mercury in Sorbtech Hg sorbent	3.8 mg
Mass balance	95%
Removal efficiency	**94%**

The thin bed of Sorbtech Hg sorbent removed an average of 94% of the mercury from the 400°F gas passing through it at 26,000 bed volumes/hr (0.13 sec. residence time), loading up to 0.10-wt% Hg (equivalent to 1,000:1 carbon to Hg) after an hour. While this was a fixed-bed test on a more-concentrated stream, rather than a duct-injection test on a less-concentrated stream, it does independently corroborate the new sorbent's ability to remove and retain a high degree of elemental mercury from a high-temperature, 400°F off-gas stream.

Preliminary Economics

The cost savings of using the new Sorbtech Hg sorbents for elemental mercury removal at coal-fired power plants could be extremely large. In quantity, the new sorbents should cost about $2,000 per ton. If injection at 1,500:1 sorbent to Hg yielded just 50% elemental mercury removal, for example, the average cost would be only $3,000 per-ton-of-mercury-removed:

$$\left(\frac{\$2{,}000}{2{,}000\ lb\ sorbent}\right) x \left(\frac{1{,}500\ lb\ sorbent}{1\ lb\ Hg\ in\ gas}\right) x \left(\frac{1\ lb\ Hg\ in\ gas}{0.50\ lb\ Hg\ removed}\right) = \$3{,}000\ /\ lb\ Hg\ removed.$$

Such costs are about one-tenth those estimated in the Reports to Congress.

Use of the new sorbents looks to be very inexpensive because:

✓ The sorbents work at the high temperatures, 400 to 300°F, available in coal-fired plants.

Because they work at high temperatures, no expensive and troublesome flue-gas cooling is required. Flue-gas cooling is expensive because of the energy consumption required by the high-pressure, dual-fluid nozzles necessary to produce fine water droplets that can evaporate within the short retrofitted distances available. Moreover, the creation of H_2SO_4 is likely and significant downstream corrosion and opacity problems, or a "blue plume" could result. And lowered temperatures are not compatible with SCR NOx-removal. The new materials lead to none of these problems, because of their apparent high-temperature reaction/adsorption abilities.

✓ The Sorbtech Hg sorbent materials are inexpensive.

While powdered activated carbon is relatively inexpensive, large quantities are required with hot flue gases. Impregnated activated carbons, containing sulfur, iodine, or chloride salts, for example, may work better, but they cost on the order of $5,000 to $10,000 per ton. The new sorbent materials described here, on the other hand, are made from relatively inexpensive material and should only cost about $2,000 per ton.

- ✓ The new sorbents exhibit fast kinetics when applied in the inexpensive duct-injection mode.

Advanced sorbents with high mercury capacities, such as impregnated carbons, usually require long gas/sorbent contact times in order to take advantage of their mercury capacity. In the real-world, this may mean that a very expensive fabric filter will have to be constructed either as an alternative to, or in addition to, the existing ESP. The new sorbents, on the other hand, appear to perform well enough in a short one-to-two-second residence time in the duct.

- ✓ Only modest injection rates appear to be required.

A great deal of utility fly ash is currently sold by utilities for cement and structural uses. If high carbon injection rates are required, not only do sorbent costs balloon, but the collected fly ash may no longer meet the specifications required for productive use and will require costly disposal. This is not a problem at the low injection rates indicated so far with the new sorbents.

- ✓ Finally, this new technology can be applied to just about any coal-fired boiler downstream configuration and can be easily coupled with other sorbents or technologies for oxidized mercury removal.

Future Plans

A development program is currently underway to optimize the new Sorbtech Hg sorbents and improve their elemental mercury removal rates to greater than 90%. This work is being partially supported by the Ohio Coal Development Office of the Ohio Department of Development and the U.S. Environmental Protection Agency. Sorbent Technologies Corporation is also actively seeking coal-fired power plant sites to demonstrate the mercury removal capabilities of the new materials.

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