# A New Non-carbon Sorbent for Hg Removal from Flue Gases

**Paper # 139**

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## ABSTRACT

TDA has developed a novel non-carbon sorbent to control mercury emissions from the flue gases of coal-fired power plants. The sorbent could be easily injected into the flue gas and could be recovered in the Particulate Control Device (PCD) along with the fly ash. Unlike the carbon materials used to date, our sorbent does not alter the properties of the by-product fly ash and render it unsuitable as a cement additive. We have demonstrated the technical feasibility of using new non-carbon sorbents for mercury removal. The sorbent achieved a much higher mercury capacity than Darco Hg sorbent (a carbon produced by Norit Americas), a benchmark sorbent in mercury emission control from the flue gases, removing over 688 μg/g at 150°C (302°F) at 95% Hg removal efficiency in a fixed-bed experimental setup under representative simulated flue gas. Our sorbent could effectively oxidize elemental $Hg^0$ to $Hg^{2+}$ (a form that can be readily removed by a wet scrubber) at temperatures as low as 220°C (428°F) under simulated conditions. Based on the success of our sorbent at bench-scale, we demonstrated the effectiveness of our sorbent using a slipstream of actual flue gas in collaboration with Apogee Scientific, Inc. at Xcel Energy's Pawnee Power Station.

## INTRODUCTION

Coal-fired power plants, along with the hazardous and municipal waste incinerators contribute over 2/3rd of the mercury emissions in the U.S. Under the current law, Hg emissions from the waste incinerators are regulated. Further, the Clean Air Mercury rule will permanently cap power plant mercury emissions in two phases: the first phase cap is 38 tons beginning in 2010, with a final cap set at 15 tons beginning in 2018. The regulations in some states, particularly those in the Northeast, require even more stringent mercury controls than those set by EPA, and the timeline is compressed. However, the cost effective removal of mercury from flue gases of coal-fired power plants is still a challenge.

Mercury is found naturally in coals throughout the world. Because it is highly volatile, when coal is burned, nearly all mercury vaporizes and exits the boiler in the flue gas. Coal-fired utility boilers emit several the mercury compounds, primarily elemental mercury ($Hg^0$), mercuric chloride ($HgCl_2$) and mercuric oxide (HgO), where the proportions depend on the characteristics of the fuel being burned and the combustion method. The particular form of mercury present in the gas plays an important role in determining the effectiveness of the control strategies. The oxidized form of mercury is by far the most easily removed, and even existing pollution control devices such as scrubbers and particulate control systems remove some of the oxidized mercury. The removal of elemental mercury is much more complex. Unfortunately, the oxidized mercury constitutes only a small fraction of the mercury in the flue gas (particularly in low-grade lignite coals).

To be practical for existing power plants a mercury abatement system must be easy to retrofit into the existing plant infrastructure, requiring only minimal capital investment. The approach that best meets this requirement is dry sorbent injection. In this process, a sorbent is injected into the flue gas, where it removes gas phase mercury. The mercury-laden sorbent is then recovered with the fly ash either by a fabric filter (FF) bag house or by an electrostatic precipitator (ESP), with little or no modifications in the existing particulate removal systems, hence minimizing the capital investment. The requirements for such a sorbent are straightforward: 1) it should be low cost, 2) it should have a high mercury capacity, 3) it must have good adsorption kinetics and 4) it should not present any environmental problems in its own right. Another less obvious but extremely important consideration is that since the sorbent is collected with the fly ash, it must not limit its normal uses. Powdered activated carbon (PAC) is the most investigated option for mercury removal. However, PACs have significant impacts on combustion by-products (fly ash properties) and air pollution control device operations.

The use of carbon sorbents can cause problems with current uses of the fly ash. A large proportion of fly ash is currently sold as an extender for Portland cement in concrete. In many concrete formulations, air bubbles are intentionally entrained into the mixture (to provide workability and freeze tolerance to the concrete) through mechanical agitation and stabilized by the addition of surfactants known as air-entraining additives (AEAs). Carbon sorbents used for contaminant control in flue gases can remain in the fly ash and interfere with the function of these AEAs. In fact, in a recent large-scale test of activated carbon sorbents in a power plant burning a low-sulfur coal and using an ESP for particulate control, carbon addition prevented use of the fly ash in concrete not only for the duration of the test, but for two weeks after carbon addition was stopped (Starns et al. 2002). Based on a modest 3 lb/MMAcf (million actual cubic feet) sorbent injection rate, the carbon content of the fly ash can exceed 1% for all types of coals, rendering them useless as a cement additive. The problem is much more serious than lost sales for the power plants. If the fly ash is not salable for concrete, it has no use at all, and immediately becomes an expensive waste problem.

TDA Research, Inc. (TDA) has developed a novel non-carbon sorbent to control mercury emissions from the flue gases of coal-fired power plants. The sorbent could be easily injected into the flue gas and could be recovered in the Particulate Control Device (PCD) along with the fly ash. Unlike the carbon materials used to date, TDA's sorbent does not alter the properties of the by-product fly ash and render it unsuitable as a cement additive. It also effectively removes both elemental and oxidized forms of mercury from flue gases.

## EXPERIMENTAL

We used a fixed-bed sorbent testing apparatus that was specifically designed for measuring mercury removal from flue gases. The sorbent reactor consists of a 1.0 cm-OD Teflon lined stainless steel or Pyrex reactor tube that contains a frit at its mid-point to support pellets. A Mellen tube furnace surrounding the reactor is used to control the temperature. The desired gases are introduced into the system through electronic mass flow controllers. After mixing in a manifold, the gas stream is preheated above the dew point of water to prevent condensation.

The mixture then passes through a saturator where water is mixed into the feed stream by a peristaltic pump. This saturator is designed to allow complete evaporation of the liquid and ensures mixing of the gases prior to exiting the device. The preheated feed mixture is combined with a mercury laden-gas stream. Mercury is introduced using permeation tubes (VICI Metronics, Inc, Santa Clara, CA). The permeation tube is a small capsule containing liquid mercury. At a constant temperature, the device releases a known concentration of the compound into a carrier flow. The temperatures of the capsules are chosen to entrain an appropriate trace amount of material into the synthetic flue gas. The preheated feed gas stream is then directed to the reactor. There is a valve system that allows the feed gases bypass the reactor and flow directly to the analytical system for accurate measurement of the feed gas composition. Mercury analysis was carried out using a Process Sentinel mercury analyzer from Genesys Labs. (Grand Junction, CO). It has a detection limit of nominally 0.1 $\mu g/m^3$ and a range of 1-999 $\mu g/m^3$ of mercury. The gas exiting the packed bed is conditioned before releasing into the environment. In early experiments, we used a series of two impingers: the first impinger contains a caustic solution to remove acid gases that may interfere with the operation of the mercury detector. The second impinger is cooled to -10°C to remove moisture. Later on we added a polymeric membrane to remove the water before the gas stream reaches the analyzers (both mercury and $SO_2$ analyzers were sensitive to water). The apparatus is fully automated and can run without an operator for long periods of time, including overnight. The sorbent test results were also confirmed with post-chemical analysis (ICP-AA). We evaluated the performance of our sorbent using the simulated flue gas composition under various operating conditions. The typical gas composition and the test conditions used are summarized in Table 1 and Table 2.

Table 1. Typical gas composition (wet basis).

| **Component** | **Vol%** |
|---|---|
| $CO_2$ | 10.0% |
| $H_2O$ | 8.0% |
| $N_2$ | 79.0% |
| $O_2$ | 2.0% |
| $SO_2$ | 10-300 ppm |
| $NO_x$ | 10-50 ppm |

Table 2. Summary of test conditions.

| **Parameter** | **Range** |
|---|---|
| Hg Inlet | 1-50 $\mu g/m^3$ |
| Temperature | 100-320$^oC$ |
| Pressure | 1-2 psig |
| GHSV | 100,000 – 2,000,000 $h^{-1}$ |
| Sorbent Particle Size | 80-150 $\mu m$ |

## RESULTS AND DISCUSSION

### Sorbent Performance in Simulated Flue Gas

Figure 1 shows typical breakthrough profiles of different Hg species for TDA's Hg sorbent. Following an inlet measurement of total Hg concentration (of 48 $\mu g/m^3$ all of which is elemental Hg), the gas flow was directed to the sorbent bed and observed an immediate decline in the Hg concentration of the flue gas. We first observed the $Hg^{2+}$ breakthrough from the bed. TDA's sorbent first converts $Hg^0$ to $Hg^{2+}$ and then removes $Hg^{2+}$ over high surface support. The removal of oxidized forms of Hg with physical adsorbents is easier. TDA's sorbent was very good in converting $Hg^0$ to $Hg^{2+}$ but its capacity for $Hg^{2+}$ was also limited. It still has reasonably high capacity for $Hg^{2+}$. At 90% removal efficiency the sorbent achieved 688 μg/g Hg capacity.

We then tested a mixture of TDA's Hg sorbent and the Darco-Hg carbon, using a mixture of 5:1 on a weight basis. This mixture achieved over 99% removal efficiency throughout the test duration. We initiated the testing with the standard gas mixture without any $SO_2$. Up to the 300 ppmv $SO_2$ introduction the sorbent combination removed 1,171 μg/g at 99% removal efficiency, and an added 1,730 μg/g after the introduction of 300 ppmv $SO_2$. At 2,500 minutes into the test, the $SO_2$ cylinder ran out, while the combined bed achieved an overall Hg capacity of 2,901 μg/g at 99% Hg removal (Figure 2).

These results show that the TDA's sorbent could either be used as a stand alone sorbent to effectively remove Hg from flue gases. It converts the $Hg^0$ to $Hg^{2+}$ very effectively; in fact the sorbent performance is limited by $Hg^{2+}$ removal capability. This makes it a good candidate to be used with other sorbents that are known to be effective for $Hg^{2+}$ removal, such as the unmodified low cost carbon sorbent. The evaluation of a mixed sorbent bed that contains 17% carbon and 83% of TDA's sorbent could achieve a very high removal performance. Due to the high oxidation activity provided by our sorbent, the carbon could be used more effectively and in much smaller quantities. Therefore, the net use of carbon and its concentration in the fly ash could be greatly reduced.

### Testing at Low Hg Concentration

We carried out most of our tests under accelerated conditions where we used a high concentration of Hg to facilitate rapid breakthroughs. In these experiments, we used 45-60 $\mu g/m^3$ of Hg, a concentration about 3 to 5 times higher than typical Hg concentrations observed in typical flue gases. It is well known that the higher concentrations could yield higher capacities (both the Hg oxidation and Hg sorption process benefit from high Hg concentration in the gas). Therefore, we evaluated our best sorbent using a flue gas Hg concentration of 15 $\mu g/m^3$. At the same time, we also reduced the gas-solid contact time of the sorbent to 5.5 milliseconds to be able to complete the evaluation of the sorbent at a reasonably short duration. At such short residence times, our sorbent could only achieve 90% Hg removal efficiency. We calculated the Hg capacity of the sorbent as 743 μg/g at 90% removal efficiency and 1,592 μg/g at 75% removal efficiency.

Figure 1. Typical test profile with TDA's Hg sorbent in simulated flue gas.

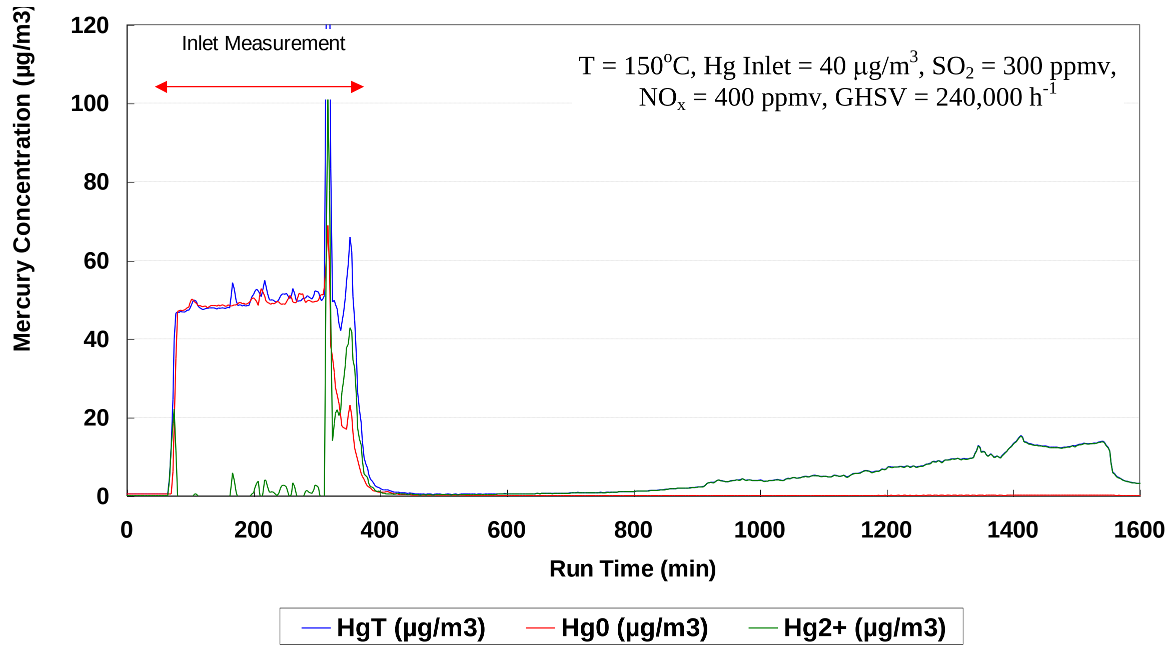
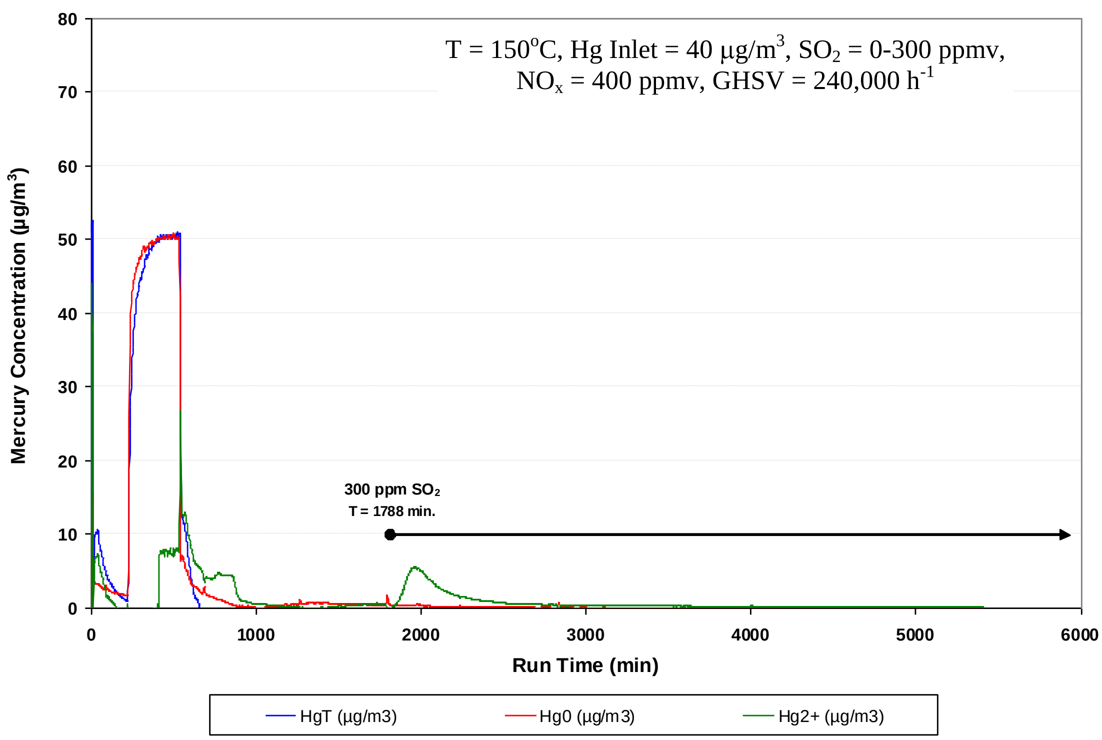
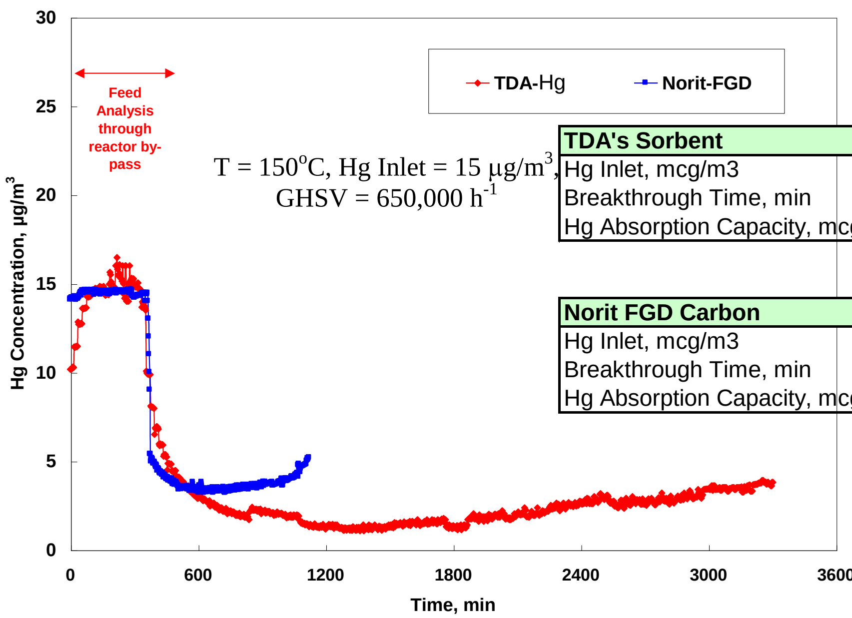



Figure 2. A 5:1 combination of TDA's Hg sorbent and Darco-Hg sorbent showing a capacity of 2910 µg/g at 99% removal efficiency in the presence of $SO_2$.



To ensure that the sorbent performance is not an artifact of the reactor, we benchmarked the performance against the Darco-Hg sorbent, a widely used sorbent for mercury control from flue gases.  As shown in Figure 3, TDA's sorbent outperformed the Darco-Hg sorbent at 150°C under identical conditions.  The Hg absorption capacity of Darco-Hg sorbent was only 275 μg/g at 70% Hg removal efficiency.  Due to the high space velocity used in the test, neither sorbent achieved removal efficiencies in excess of 95%.  Although the test conditions does not favor the carbon sorbent due to the lack of flue gas oxidants, these results clearly show that TDA's sorbent shows a lot of potential.

Figure 3. Comparison of TDA's sorbent with Darco-Hg sorbent with simulated flue gas.




| | Hg Removal Efficiency | |
|---|---|---|
| **TDA's Sorbent** | **90%** | **75%** |
| Hg Inlet, mcg/m3 | 15.1 | 15.1 |
| Breakthrough Time, min | 1377 | 2952 |
| Hg Absorption Capacity, mcg/g | 743 | 1592 |

| | Hg Removal Efficiency | |
|---|---|---|
| **Norit FGD Carbon** | **90%** | **75%** |
| Hg Inlet, mcg/m3 | 14.5 | 14.5 |
| Breakthrough Time, min | N/A | 536 |
| Hg Absorption Capacity, mcg/g | N/A | 278 |

## Slipstream Demonstration

To assess the full benefit of the technology, we carried out an evaluation of our sorbent using a slipstream of a real flue gas.  We subcontracted Apogee Scientific to evaluate the performance of selected sorbents in the PoCT systems in a relevant environment (i.e., injected as a dry sorbent in a flow reactor).  The unit was hosted at Xcel Energy's Pawnee Station at Fort Morgan, CO (Figure 4).  The plant burns low sulfur PRB coals.

Figure 4. Xcel Energy's Pawnee Power plant at Fort Morgan, CO.

The overall goal of this evaluation was to assess the effectiveness of TDA Research's novel Hg sorbent for mercury removal in the flue gas for plants burning Powder River Basin sub bituminous coal (PRB). Slipstream injection tests were conducted at a host utility upstream of the baghouse. Batch injection testing was conducted using EPRI's multi-Pollution Control Test (PoCT) system configured as a reverse air pulse jet bag house. Mercury removal across the bag house was measured with and without sorbent injection. This report presents the results from the field evaluations. The specific objective of this test program was to provide mercury removal numbers with each sorbent injected into the bag house. The PoCT system was setup to give mercury removal numbers across a fabric filter bag that has a flow of ~5 Acfm. Apogee Scientifics' mercury continuous emissions monitor (Hg CEM) was used during this program to provide real-time measurements of mercury concentration. The Hg CEM was configured with dual measurement channels that were used to measure at two different extraction locations (inlet and outlet of bag house number 2).

The host utility is located in the West and burns a Powder River Basin sub bituminous coal. The boiler is a conventional PC rated at 508 MW. A pulse-jet baghouse controls particulate emissions on Unit 1. Mercury measurements were made upstream of Unit 1's baghouse. According to the EPA 1999 ICR Database, the total inlet mercury concentration for Unit 1 was around 3.5 $\mu g/Nm^3$, although from baseline testing current mercury values range from 8 to 13 $\mu g/Nm^3$.

We carried out a baseline analysis with an activated carbon sorbent -either with Darco Hg or Darco Hg-LH (a halogen impregnated carbon) before injecting the TDA sorbent. We initially evaluated all sorbents at a standard injection rate of 1 lb/MMAcf. Both versions of the Darco sorbent worked very well. The unexpectedly good performance of the un-impregnated Darco Hg sorbent could be explained by the unexpectedly high concentration of oxidized Hg species in the flue gas (more than half of the Hg was in the oxidized form). Figure 5 shows a direct comparison of the non-carbon TDA Hg sorbent with these baseline formulations. In these tests, TDA sorbent removed 56% of the Hg while achieving 398 μg/g Hg capacity. This was lower than what we observed in our bench-scale tests. We believe that it is related to the very small amounts of sorbent used in the injection tests allowing a large Hg leakage. TDA Hg sorbent has a density of 1.18 g/cc, which is more than 3 times denser than the Darco Hg sorbent. The way the test was conducted at a fixed mass flow rate of sorbents; TDA sorbent did not have much coverage over the filter material in the baghouse. Thus, we believe the higher than expected Hg leakage was due to channeling from insufficient amount of sorbent accumulation over the filter media. In a fourth test, we also evaluated a 3:1 mixture of the TDA and Darco Hg sorbent. As in agreement with our laboratory tests, we showed an improvement in Hg removal efficiency and the capacity (74% removal efficiency was achieved). In this configuration, even though activated carbon is added, its amount and as a result its impact on the fly ash was reduced by 75%.

Figure 5. Slip stream testing of TDA's Hg sorbent at an injection rate of 1 lb/MMAcf.

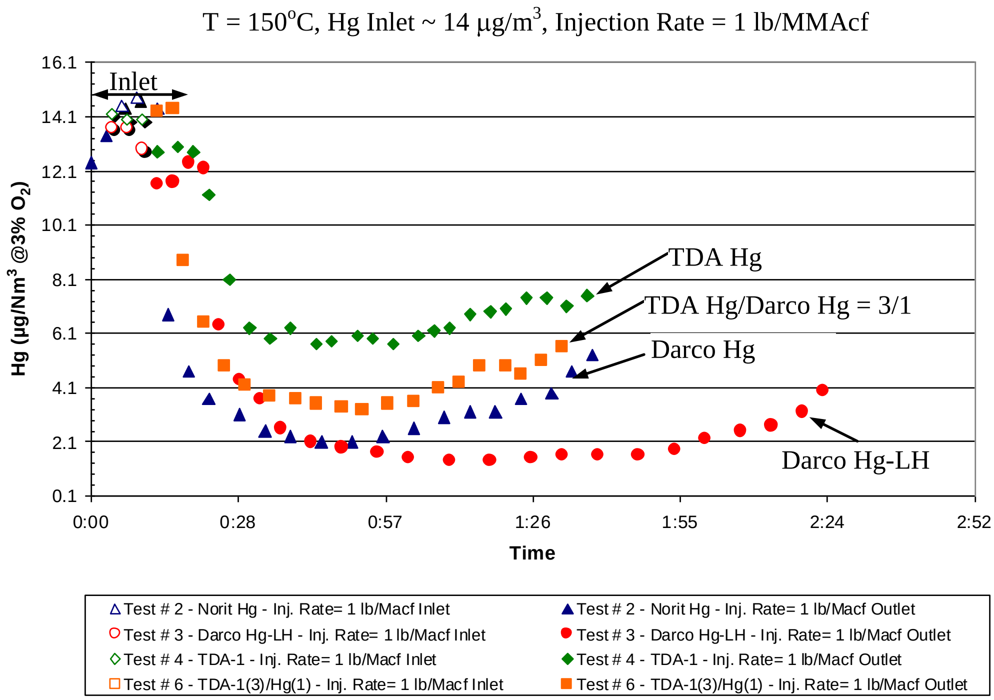
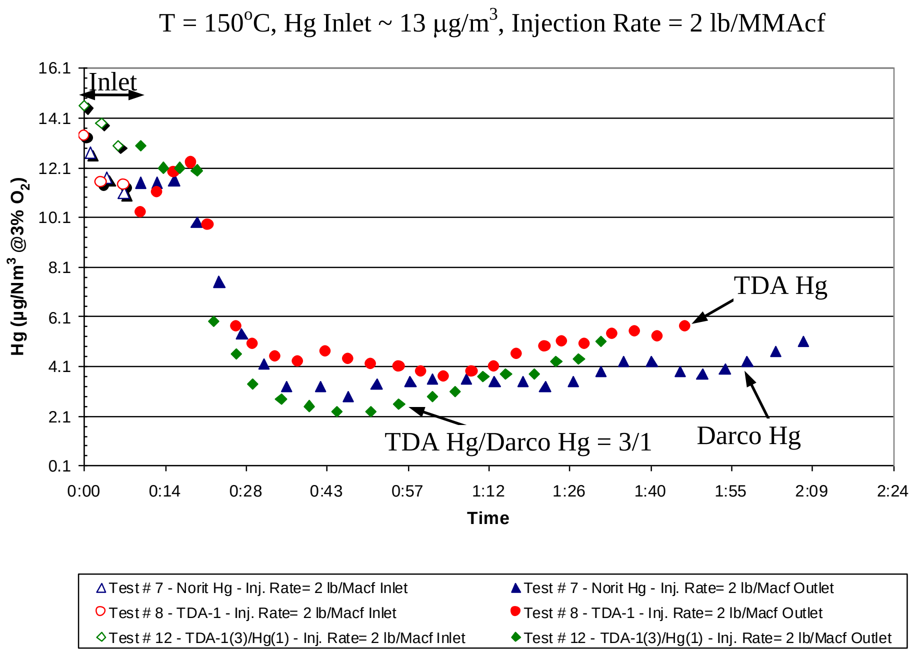



Figure 6. Slip stream testing of TDA's Hg sorbent at an injection rate of 2 lb/MMAcf.



In order to address the issue of channeling we increased the sorbent injection rate to 2 lb/MMAcf for all sorbents in the later tests. As we increased the sorbent injection rate, we observed that the TDA Hg sorbent achieved a very comparable removal performance to that of the Darco Hg sorbent (Figure 6). When we combined the TDA sorbent with the Darco Hg at a mass ratio of 3:1, the mixture achieved 81% removal efficiency, which was better than that can be achieved by the Darco Hg sorbent alone (75%).

## Sorbent Characterization

### *Foam Index Tests*

The foam index test (Gao et al. 1997) is used to determine whether a particular fly ash is suitable for use in cement. We tested our sorbent to make sure that it does not increase the foam index of fly ash. This gives our sorbents an additional advantage over carbon sorbents for mercury abatement. Before fly ash can be used in the manufacture of cement, it must pass several quality control tests. One important such test is to determine the amount of air-entraining agent required to achieve a stable foam. This is determined by a titration procedure, in which the air-entraining agent is added to an aqueous mixture of fly ash and Portland cement in small amounts until a stable foam can form.

Foam index testing of TDA's Hg sorbent and a baseline commercial carbon (Darco Hg) sorbent were carried out at Tribo Flow Separations (Lexington, KY) using the automated foam index test ($^{A}$FIT™) instrument. The two samples were mixed into a coal combustion ash (4.4% LOI) at concentrations of 1%, 3% and 5% and then the foam index values of these mixtures and of the ash by itself were measured using the $^{A}$FIT™ instrument while using two 'standard' air entraining agents (AEA): dodecylbenzenesulfonic acid, sodium salt (DDBS) and sodium lauryl sulfate (SLS). Both of the AEA's were used in diluted form (100:1 = H2O:AEA) during AFIT™ testing.

Foam index test results are presented on the basis of pure AEA usage per kg of sample tested. These uptake values are directly related to the amount of AEA required to instill stable and proper air contents when using pozzolans with or without the presence of mercury sorbents or other material modifiers into concrete mixes. To measure the amount of AEA to be used in concrete mixes containing combustion ash it would also be necessary to perform $^{A}$FIT™ testing of "ash plus cement plus sorbent" mixtures. Nevertheless, the AFIT™ test results presented in Table 3 and Figure 7 give a direct measure of the extent to which AEA usage would change as the amount of sorbent in the combustion ash changed.

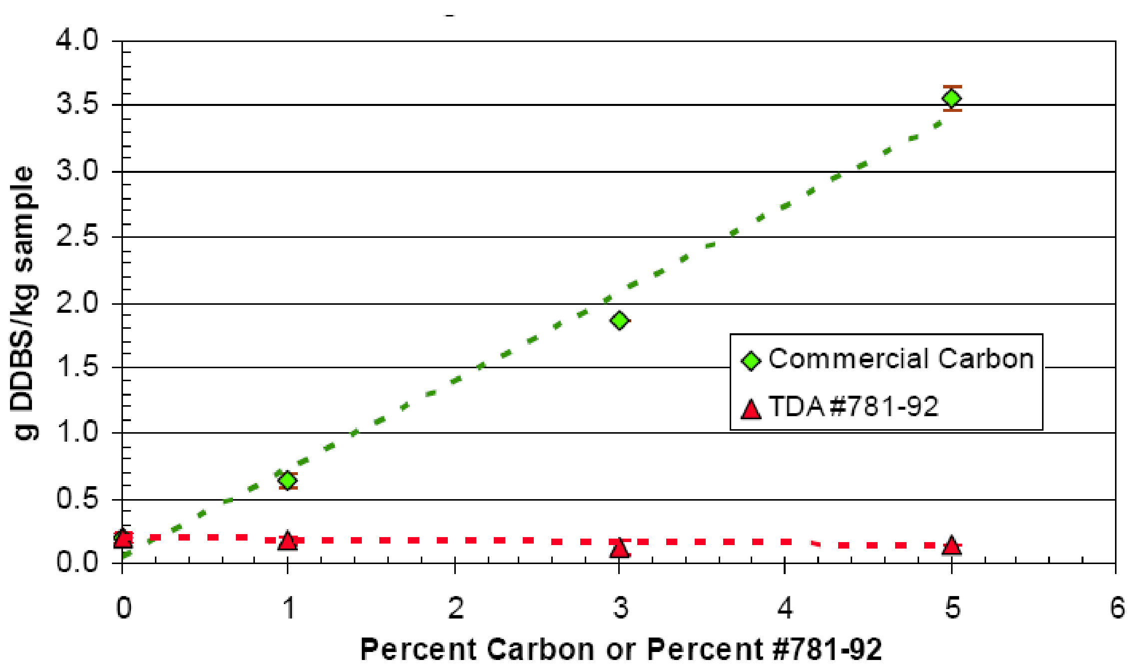
The data in Table 3 and Figure 7 show that the addition of TDA's Hg sorbent (#781-92) into the combustion ash did not change the capacity of the "ash plus sorbent" mixture to absorb AEA's, either DDBS or SLS, i.e. foam index values were unchanged as the amount of TDA Hg sorbent was increased from 0%-5%. Oppositely, the data in Table 3 and Figure 7 show that the foam index increased linearly as Commercial Carbon concentrations were increased between 0%-5%; at 5% Commercial Carbon the amount of AEA needed to produce dynamically stable air bubbles was between 15-20 times greater than when no Commercial Carbon was mixed into the combustion ash. These differences are significant because the application of AEA into concrete mixes is expensive and, more importantly, determines whether the concrete will meet engineering specifications.

Table 3. Automated foam index test results for a coal combustion ash with sorbents added.

| Sorbent added | % Sorbent Added | AEA Type* | Foam Index g AEA/kg ash | ± 2 Sigma g AEA/kg ash |
|---|---|---|---|---|
| None | 0 | DDBS | 0.21 | 0.04 |
| Commercial Carbon | 1 | DDBS | 0.63 | 0.05 |
| Commercial Carbon | 3 | DDBS | 1.86 | 0.00 |
| Commercial Carbon | 5 | DDBS | 3.56 | 0.09 |
| | | | | |
| None | 0 | DDBS | 0.21 | 0.04 |
| #781-92 | 1 | DDBS | 0.18 | 0.03 |
| #781-92 | 3 | DDBS | 0.13 | 0.05 |
| #781-92 | 5 | DDBS | 0.15 | 0.00 |
| | | | | |
| None | 0 | SLS | 0.28 | 0.06 |
| Commercial Carbon | 5 | SLS | 5.23 | 0.61 |
| #781-92 | 5 | SLS | 0.22 | 0.02 |

* DDBS = dodecylbenzenesulfonic acid, sodium salt
* SLS = sodium lauryl sulfate

Figure 7. Automated foam index test results for DDBS usage in a combustion ash with and without two different mercury sorbents.




***Leaching Tests – Synthetic Groundwater Leaching Procedure (SGLP)***

The stability of the absorbed mercury on the sorbent/fly ash is a factor to be considered in the sorbent selection for mercury abatement. We sent mercury-laden samples to an independent lab to determine the permanence of the mercury on the sorbent using the synthetic groundwater leaching procedure (SGLP; Hassett 1998). This procedure exposes the fly ash containing the mercury-laden sorbent to a synthetic groundwater. The groundwater generally contains Na, $SO_4$, and $HCO_3$, as well as other minerals that may be present in the groundwater of the location of interest. The pH is adjusted to mimic the groundwater where the fly ash is to be stored, disposed of, or used. Three different lengths of tests may be performed. The shortest test is 18 hours, during which the fly ash is exposed to the synthetic groundwater in a 20:1 liquid: solids ratio, with end-over-end agitation. At the end of 18 hours, the mixture is filtered, and the liquid analyzed for the presence of mercury, or other metal species of concern. The longer tests run for 30 or 60 days, with the same procedure.

Our Hg sorbent taken after the adsorption test containing 0.1% adsorbed Hg was mixed with deionized water in the ratio of L/S = 20. The sorbent water mixture was agitated for 18 hr and filtered using a Millipore Type AW prefilter, AW0304700. The leachate (filtrate – DI water) was then sent to Huffman Laboratories in Golden, CO for analysis of Hg and the active materials present in the sorbent. A control sample of the DI water used was also sent to the laboratory for getting a baseline. The SGLP test conditions are summarized in Table 4.

Table 4. SGLP test conditions.

| SGLP Test Conditions | | | |
|---|---|---|---|
| Sorbent amount used | | 0.6 | g |
| DI water used for | | 12 | mL |
| for leaching | | | |
| Amount present in the sorbent | | | |
| Hg Present | 0.6 | mg | 0.1% |

The test results from Huffman Laboratories are provided in Table 5. The adsorbed Hg is held strongly on the sorbent and only leached very small amount, while the active materials did not leach from the sorbent surface. These results prove that TDA's Hg sorbent is stable after Hg adsorption and does not adversely affect the environment when present in the fly ash.

Table 5. SGLP test results.

| Element | Present in leachate (ppm) | Max. Possible (ppm) | % leached |
|---|---|---|---|
| Hg | 0.52 | 50 | 1.04% |

## SUMMARY

TDA has developed a novel non-carbon sorbent to control mercury emissions from the flue gases of coal-fired power plants. The sorbent could be easily injected into the flue gas and could be recovered in the Particulate Control Device (PCD) along with the fly ash. Unlike the carbon materials used to date, our sorbent does not alter the properties of the by-product fly ash and render it unsuitable as a cement additive. We have demonstrated the technical feasibility of using new non-carbon sorbents for mercury removal in both bench-scale sorbent evaluations using simulated flue gases and a slip stream testing in an actual power plant using real flue gas. We estimate the cost of our sorbent to be $1-2/lb when produced in large quantities needed for the power plant applications. Our sorbent could effectively oxidize elemental $Hg^0$ to $Hg^{2+}$ (a form that can be readily removed by a wet scrubber) at temperatures as low as 220$^oC$ (428$^oF$) under simulated conditions. TDA Hg sorbent could be used by itself or as a mixture with a baseline carbon (such as Darco Hg sorbent) to achieve control of elemental Hg emissions. The key benefit is that TDA sorbent will have minimal impact on the properties of fly ash. Even when mixed with carbon at a 3:1 ratio, the carbon contamination of fly ash could be greatly reduced (by a factor of four). The Hg removal mechanism also is suitable for high temperature operation with proven effectiveness up to 245$^oC$ (475$^oF$).

## ACKNOWLEDGEMENTS

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## REFERENCES

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