

SORBENTS THAT REMOVE MERCURY FROM FLUE GASES

The Problem

Coal-fired power plants currently emit about 40% of the total U.S. man-made mercury emissions; about 41 tons/year. Therefore, the U.S. Environmental Protection Agency (EPA) will require utilities to reduce mercury emissions from power plants using maximum achievable control technology. However, the cost and effectiveness of existing mercury control technologies are still uncertain. The ideal mercury abatement system would be easy to retrofit into the existing coal-fired electric utilities. One attractive approach would be dry-sorbent injection where the sorbent injected into the flue gas reacts with gas phase mercury and the mercury-laden sorbent is removed with the fly ash either by a fabric filter or by an electrostatic precipitator (ESP). The requirements for such a sorbent are straightforward: 1) it should be low cost, 2) it should have a high mercury capacity, and 3) it should not present any environmental problems in its own right. Another less obvious but very important consideration is that since the sorbent is collected with the fly ash, it must not prevent the normal uses of fly ash.

Several physical adsorbents, particularly activated carbons, can remove mercury from flue gases produced by coal combustion^{1,2}. However, activated carbons are non-selective adsorbents; most of the flue gas components adsorb on carbon, competing with mercury and severely reducing their efficiency. To improve the adsorption capacity, it is common to chemically modify the activated carbons with various chemical promoters including sulfur, iodine, chlorine and nitric acid, although the carbon treatment processes significantly increase the cost of the sorbent (chemically modified carbons costs about 4 times as much as the unmodified carbon)³. As a result, both for promoted and unpromoted carbons, the projected annual cost of abatement is high in the order of \$38,000 per pound of mercury removed (based on the combined operating and annualized capital costs) or over \$4 million per year for a 250 MW power plant⁴. In fact, all these estimates understate the difficulties and costs associated with using carbon-based sorbents. Much of the fly ash collected in the particulate control module is sold as an extender to Portland cement: fly ash can replace as much as 80% of the cement in some grades. However, fly ash that contains carbon is not suitable for use in cement. The problem is much more serious than lost sales. 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) is developing a new sorbent/catalyst combination that can capture and remove all mercury species. The sorbent is made of non-carbon based materials and has a high mercury absorption capacity, thus will not alter the properties of the fly ash. The sorbent can be produced as an injectable powder for easy integration into the existing power plant infrastructure. Below we describe the initial testing results of the new sorbent material.

Experiments

Several formulations were screened to measure to their physical properties, including porosity, surface area, crush strength of the pellet and active material content⁵. In the selection of proper active material and support, the material costs were taken into consideration. The choice of substrate materials included conventional supports, which are low-cost and have high surface area (150 to 580 m²/g measured by the manufacturers). The best formulations with the desired physical properties were tested to determine their sulfur removal performance under simulated flue gas conditions.

A fixed-bed reactor was used to measure sorbent performance for removing mercury from flue gases. The sorbent reactor consists of a 2.5 cm-OD quartz-lined stainless steel reactor tube that contains a frit at its mid-point to support monoliths or pellets. A Mellen tube furnace surrounding the reactor was used to control the temperature. The desired gases were 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 was mixed into the feed stream by a peristaltic pump. The preheated feed mixture was combined with a mercury laden-gas stream. Mercury was introduced using permeation tubes (VICI Metronics, Inc, CA), blending trace amounts of mercury into the synthetic flue gas. The preheated feed gas stream was then directed to the reactor. A valve system also allowed the feed gases bypass the reactor and flow directly to the analytical system for accurate measurement of the feed gas composition. The gas exiting the packed bed was conditioned before releasing into the environment.

To analyze for mercury, a Genesys Laboratory Systems Process Sentinel mercury vapor detector was used with a detection limit of nominally 1.0 $\mu\text{g}/\text{m}^3$ and a range of 1-999 $\mu\text{g}/\text{m}^3$ of mercury. After the tests, selected sorbent samples were sent to analysis in a local laboratory for chemical analysis using Inductively Coupled Plasma Atomic Absorption to confirm to mercury uptake of the sorbents.

Performance

The sorbent/catalyst combination is designed to be injected into the flue gas stream after the air preheater. At the injection location the flue gas temperature may range from 120 to 180°C, depending on the efficiency of the economizer and air pre-heater (a recuperative heat exchanger that heats the air to the boiler). Higher temperatures promote faster kinetics for mercury oxidation reaction. The removal process of mercury, however, favors lower temperatures, where lower equilibrium Hg concentration can be achieved (i.e., high removal efficiency). The preliminary bench-scale experiments were carried out to measure mercury absorption capacity of the sorbent at temperatures that closely simulate the temperatures of the cold-side and warm-side of a typical particulate control unit. In a typical test, we used a 2% O₂, 6% CO₂, 8% H₂O and 84% N₂ on volume basis to simulate the flue gas.

The sorbent achieved mercury absorption capacities ranging from 7.5 to 11.0 mg/g depending very strongly on the temperature and gas hourly space velocity selected for testing. Figure 1 shows the mercury breakthrough profile over the sorbent at 140°C under the flow of a sulfur-free simulated flue gas. The gas hourly space velocity and mercury inlet concentration through the test were maintained at 60,000 h⁻¹ and 0.12 mg/m³, respectively. The mercury absorption capacity of the sorbent was calculated as 10.85

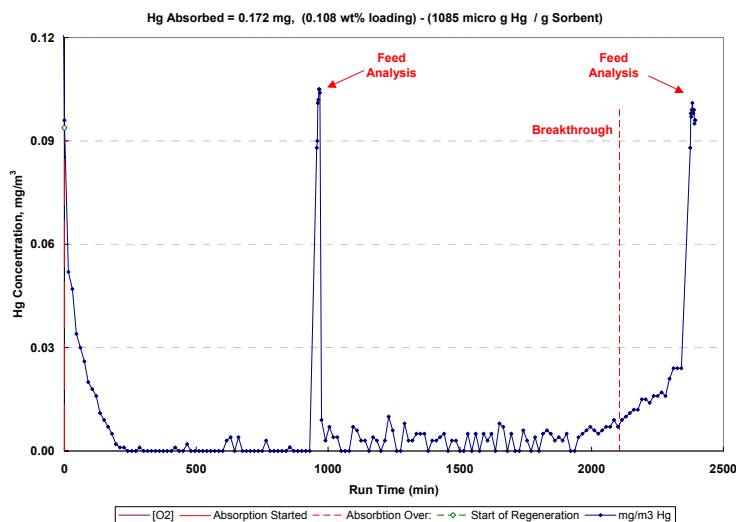


Figure 1. Mercury breakthrough profile over TDA sorbent with simulated flue gas containing 2% O₂, 6% CO₂, 8% H₂O and 84% N₂ on volume basis. Hg Inlet Conc. = 0.12 $\mu\text{g}/\text{m}^3$, T = 140°C, GHSV = 60,000 h⁻¹.

mg/g at a pre-breakthrough level. Test result also suggests that the sorbent is capable of achieving over 95% mercury removal efficiency. The capacity of the sorbent is among the highest reported in the literature⁶.

Although effective flue gas desulfurization technologies are available that can reduce the sulfur emissions to very low levels, some amount of sulfur is likely to be present in the flue gas. Bench-scale experiments with sulfur containing simulated flue gas were carried out to demonstrate the mercury removal potential of the sorbent in the presence of sulfur. For these experiments, flue gas streams containing 3 and 300 ppmv sulfur dioxide (SO₂) was passed through the sorbent bed maintained at 140°C. These sulfur concentrations represents a flue gas stream with upstream Flue Gas Desulfurization and a flue gas generated with low sulfur coal combustion with no upstream desulfurization.

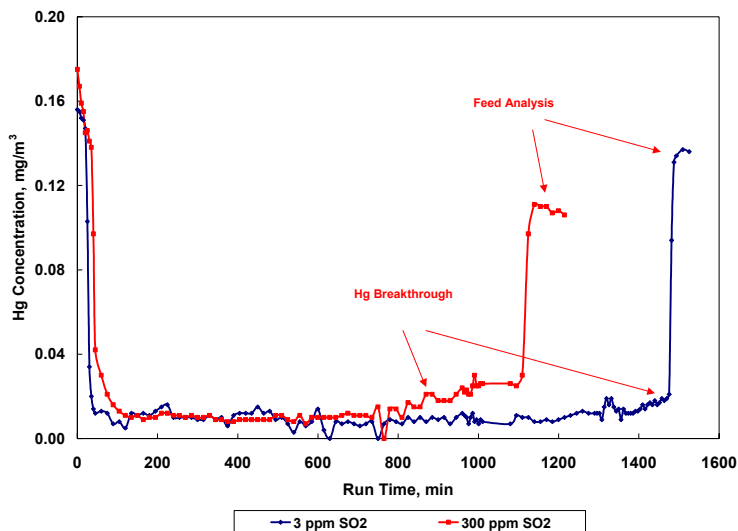


Figure 2. Mercury breakthrough profile over TDA sorbent with simulated flue gas containing 2% O₂, 6% CO₂, 8% H₂O and 84% N₂ on volume basis. Hg Inlet Conc.= 0.18 µg/m³, T= 140°C, GHSV=650,000 h⁻¹.

The sulfur tests were carried out at 650,000 h⁻¹ gas hourly space velocity, simulating the very short gas-solid contact times in dry sorbent injection systems. Table 1 shows the mercury absorption capacity of the sorbent at different SO₂ inlet concentrations. Although the mercury capacity of the sorbent is reduced as the sulfur level of the flue gas increased, the sorbent performed exceptionally well even in the presence of 300 ppmv SO₂ in the flue gas.

Table 1. Effect of SO₂ concentration on the pre-breakthrough mercury absorption capacity of the sorbent.

SO ₂ Concentration (ppmv)	Hg Absorption Capacity (microgram/g)
3	966
300	648

The preliminary bench-scale tests suggest that TDA's sorbent shows promise to effectively control mercury emissions even in high sulfur flue gas streams.

Acknowledgment

Part of this work was supported by the U.S. Department of Energy, under contract DE-FG02-03ER83855.

References

- Carey, T.R., Hargrove J., Richardson, R., Meserole, F., **1997**, *Proceedings of the Air Waste Management Meeting*, Paper No. 97-WA72A05, 90th AWMA, Toronto, Canada.
- Miller, S.J., Laudal, D.L., Chang, R., Bergman, P.D., **1994**, *Proceedings of the Air Waste Management Meeting*, Cincinnati, OH.
- Sjostrom, S., Smith, T., Hunt, R., Chang, R., Brown T., **1998**, *Proceedings of the Air Waste Management Meeting*, San Diego, CA.

4. U.S. EPA, **1997**, *Mercury Study Report to Congress*, EPA-452/R-97.
5. Alptekin, G.O., Hitch, B., Dubovik, M., and Cesario, M., **2004**, Proceedings of 19th Western Coal Symposium, Billings, MO.
6. Granite, E., Pennline, H., Hragis, R., **2000**, *Ind. Eng. Chem. Res.*, 39, 1020.

For further information contact:

Dr. Gokhan Alptekin
(303) 940-2349
galptekin@tda.com