Catalyst Additives to Enhance Mercury Oxidation and Capture

Quarterly Report

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Abstract

Preliminary research has shown that SCR catalysts employed for nitrogen-oxide reduction can effectively oxidize mercury. This report discusses initial results from fundamental investigations into the behavior of mercury species in the presence of SCR catalysts at Southern Research Institute. The testing was performed at Southern Research's Catalyst Test Facility, a bench-scale reactor capable of simulating gas-phase reactions occurring in coal-fired utility pollution-control equipment.   Three different SCR catalysts are currently being studied in this project – honeycomb-type, plate-type, and a hybrid-type catalyst. The catalysts were manufactured and supplied by Cormetech Inc., Hitachi America Ltd., and Haldor-Topsoe Inc., respectively. Parametric testing was performed to investigate the contribution of flue-gas chemistry on mercury oxidation via SCR catalysts. Methods and procedures for experimental testing continue to be developed to produce the highest quality mercury-oxidation data.

Most experiments so far have focused on testing the catalysts in a simulated Powder River Basin (PRB) flue-gas environment, which contains lower sulfur and chlorine than produced by other coals. Future work to characterize flue gas simulations typically derived from low and high sulfur bituminous coal will be performed in a stepwise manner, to avoid the constant interruptions in testing that occur when leaks in the system are generated during temperature transitions. Specifically, chlorine concentration vs. mercury oxidation graph will be developed for each catalyst. The contributions of temperature and later sulfur will be investigated after this is complete. Also, last quarter's tests showed a potential linear relationship between SO_3 conversion and mercury oxidation. As a result, SO3 samples will be taken more frequently to investigate each catalyst's ability to selectively oxidize mercury.

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Introduction

The objective of this project is to investigate the enhancement of elemental-mercury oxidation in coal-fired flue gas through catalysis. In addition to testing various catalyst materials, fundamental mechanisms associated with enhanced Hg-oxidation on SCR catalysts are being investigated. Where possible, Southern Research will develop semi-empirical mechanistic model(s) or correlations describing the mechanisms associated with catalysis-enhanced mercury oxidation. Results from the project will contribute to a greater understanding of mercury oxidation in flue gas.

Executive Summary

This Quarter, Southern Research Institute continues bench-scale reactor studies to evaluate the behavior of vapor-phase mercury in the presence of Selective Catalytic Reduction (SCR) catalysts. SCR catalysts are employed in coal-fired power plants for the reduction of nitrogen oxide (NO_x) emissions, but SCR catalysts also affect the speciation of other gases, such as mercury. Mercury primarily exists in two-different forms in coal-derived flue gas, $HgCl_2$ and the elemental form, and each type behaves somewhat differently in the "back-end" pollution control equipment of power plants. Oxidized mercury is readily captured in some of the commonly employed pollution control devices, such as wet scrubbers, while elemental mercury can be more difficult to capture. Therefore, a low-cost method of oxidizing mercury upstream of the wet scrubber is desired for coal-fired power plants that possess a wet scrubber. One of the best options would be a multi-pollutant solution, such as SCR catalysts for NO_x reduction and mercury oxidation, followed by a wet scrubber for mercury and SO_2 capture downstream.

The Catalyst Test Facility (CTF) continues to be used to derive fundamental kinetic information about each catalyst investigated for mercury oxidation and capture. The CTF is described and illustrated in this quarterly report. At the core of the CTF is an extensive flue-gas simulation, gas flow, and metering system. Catalyst samples are supported in a 1-½" square (for honeycomb-type and hybrid catalysts) or 1-¼" x 2" rectangular (for plate-type) Pyrex reactor, through which the entire gas flow must pass. The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO, SO_2, SO_3, and $Hg°$, in concentrations representative of that found in flue gases of existing power plants, burning specific coal types.

The simulated flue gas originates from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of precision mass-flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system with a PS Analytical 10.534 Mercury Calibration System, which consists of a reservoir containing an inert substrate impregnated with elemental mercury maintained at constant temperature. The mercury reservoir supplies a saturated stream of elemental mercury which is diluted before mixing with the other gases. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3-inch diameter by 3-feet long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place.

Bench-scale SCR catalyst tests were conducted to elucidate the relationship between the SCR catalysts and mercury speciation under particular flue-gas environments. The testing procedures were established in the last quarter of 2004 and continue to be used during the current

experiments. These procedures were described in the January 2005 Quarterly Report. The procedures described in that report were adjusted, based on discoveries made in the first quarter of 2005, described in the April 2005 Quarterly Report, and the test procedures were adapted again in the last quarter (2nd Quarter of 2005). Previously, it was discovered that ammonia greatly inhibited the oxidation of mercury. Comparative graphs are presented in this report. Simulated PRB flue gas was the main gas investigated in last quarter. All of the catalysts showed very low mercury oxidation which is probably due to the low chlorine concentrations (5 ppm). Under PRB flue gas conditions, the plate- and hybrid-type catalysts oxidized a larger percentage of the mercury than the honeycomb-type catalyst. Interestingly, the plate- and hybrid-type were also the only catalysts that significantly converted SO_2 to SO_3.

In subsequent quarters, a chlorine concentration vs. mercury oxidation correlation will be developed for each catalyst. Hydrochloric acid vapor has been shown to be the primary promoter of mercury oxidation across SCR catalysts, under unaltered coal-fired flue gas. Each catalyst will be tested across the range of HCl concentrations that are expected to be produced from coals fired at full-scale power plants. Also, the propensity of each catalyst to oxidize SO_2 as well as mercury will be more closely investigated.

Experimental

Figures 1-3 show pictures of the CTF's quartz furnace (micro-reactor), gas-conditioning bubblers for mercury speciation and stabilization prior to mercury monitoring, flue-gas continuous emission monitors (CEMs), and gas-flow control systems. Both elemental and total mercury are measured at the outlet of the CTF.
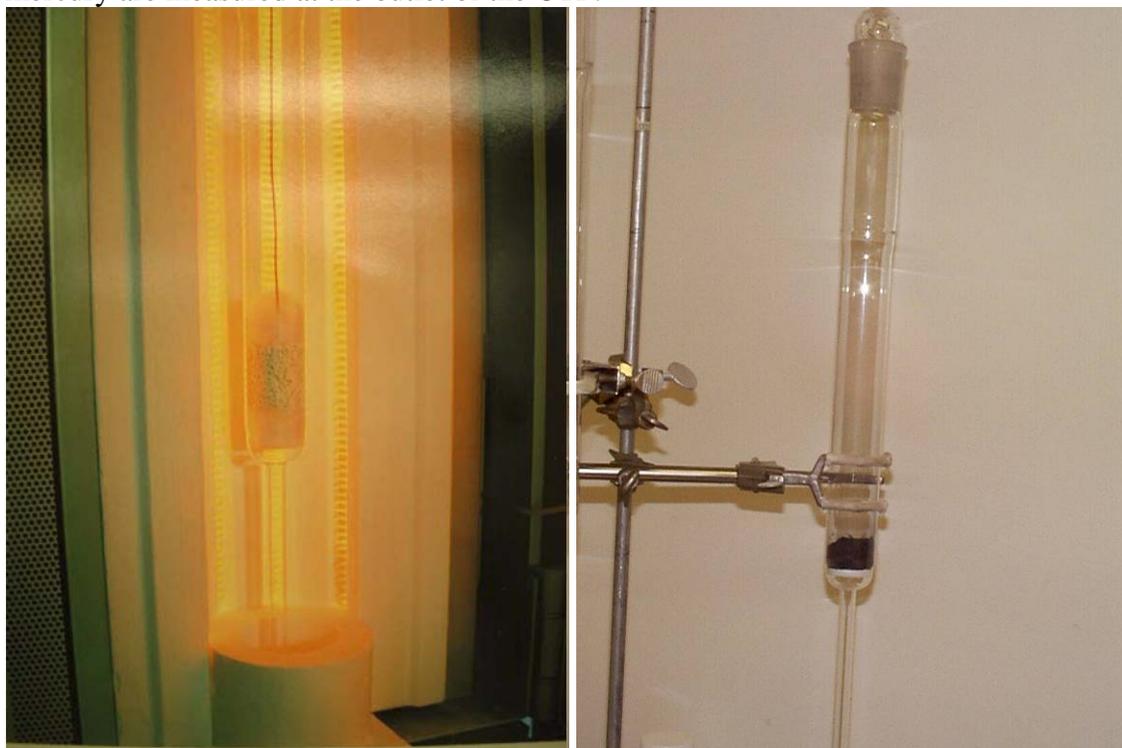
Figure 1. CTF quartz furnace at ~1000 °C (left) and outside of furnace (right).

Figure 2. Catalyst Test Facility (CTF).
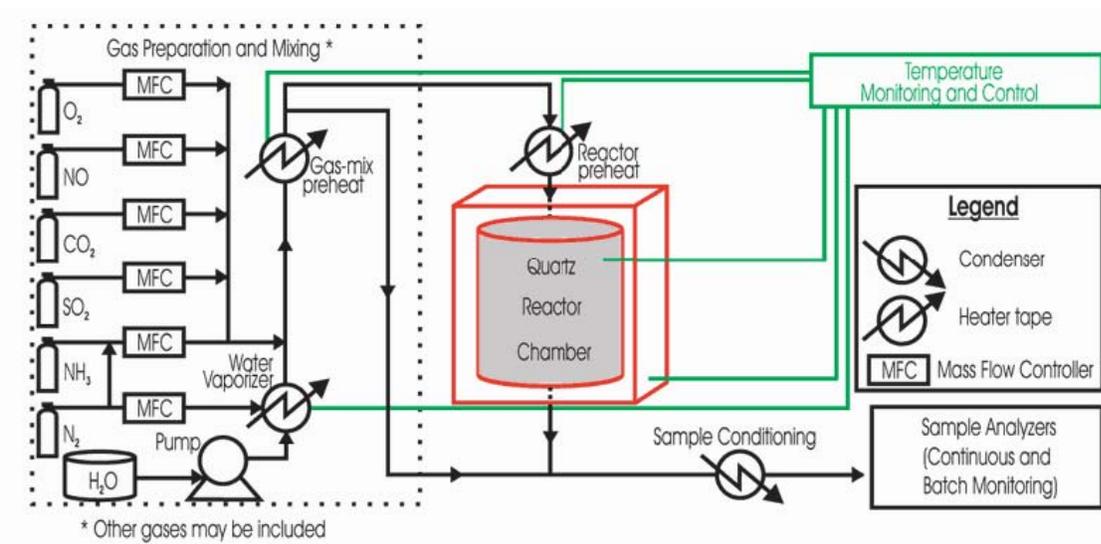
Figure 3. CTF gas-flow system.

The CTF simulates particulate-free flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO_x, SO_2, SO_3, and $Hg°$, in concentrations that exist in the flue gases of existing power plants, burning specific coal types. The simulated flue gas originates from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of mass flow controllers. The appropriate moisture content is

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generated through precise control of water evaporation. Mercury is added to the system with a PS Analytical 10.534 Mercury Calibration System, which consists of a reservoir containing an inert substrate impregnated with elemental mercury maintained at constant temperature. The mercury reservoir supplies a saturated stream of elemental mercury which is diluted before mixing with the other gases. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3-inch diameter by 3-foot long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place. Examples of the three different catalyst types are shown in Figure 4.
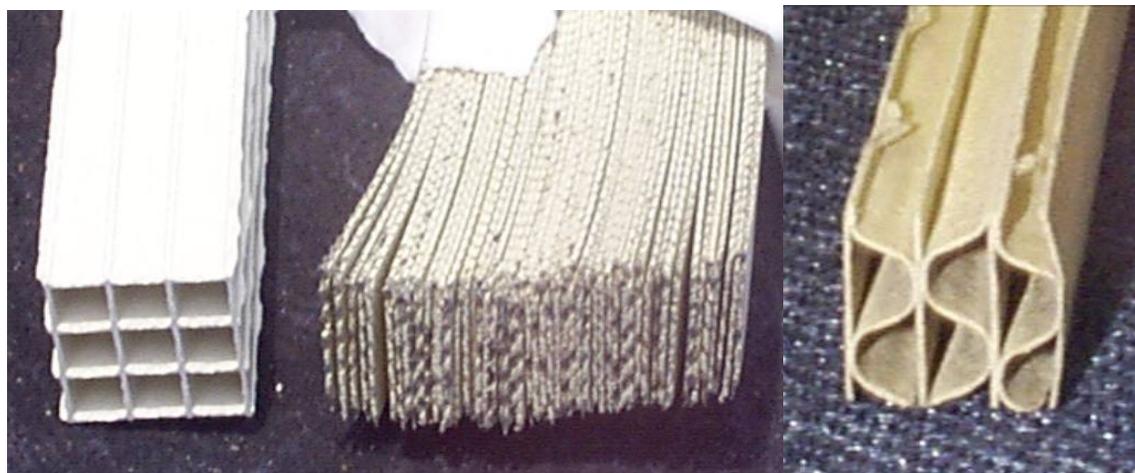
Figure 4. From left to right, honeycomb, plate, and hybrid SCR catalysts.

The majority (i.e., over 95%) of NO_x in the flue gas of coal-fired boiler systems is in the form of NO. Hence, NO is generally used in this work to simulate the NO_x in the flue gas, except for experiments specifically conducted to observe the effect of NO_2. In such cases, mixed NO/NO_2 gas bottles will be used to simulate the NO_x in the flue gas. With only NO in the flue gas, the NO_x reduction reaction is simplified to the following:

$$4NO + 4NH_3 + O_2 \; 4N_2 + 6H_2O \qquad\qquad (1)$$

All heated sections of the micro-reactor within the CTF system are made of quartz glass to limit side reactions that might occur as a result of wall effects. A semi-continuous emission monitor (SCEM) is employed to detect the mercury levels exiting the reaction chamber. A gas-conditioning system is used to convert all Hg into the elemental form, for detection using a combined gold-trap and atomic fluorescence monitor. A Tekran Model 2573A Mercury Vapor Analyzer is used to detect the elemental mercury. Along with mercury, simultaneous measurements of oxygen, carbon dioxide, nitrogen oxides, and sulfur dioxide are made using continuous emission monitors.

For details concerning the validation and operation of the CTF, refer to the March 04 DOE Quarterly Report for the Calcium-Based Hg-Sorbents project conducted at Southern Research Institute [1] and a previous Quarterly Report on this project [2].

All data in this report was generated using simulated PRB flue gas.

Table 1. Test Conditions for PRB Flue Gas.

Parameter	Value	Units
Temperature	650, 700, and 750	°F
Flow rate	7.5	slpm (@ 70°F and 1 atm)
Gas Concentrations	Simulated Powder River Basin Flue Gas	
Oxygen	5	% (dry, by volume)
Carbon Dioxide	15	% (dry, by volume)
Nitric Oxide	300	ppm (dry, by volume)
Ammonia	0/300	ppm (dry, by volume)
Sulfur Dioxide	500	ppm (dry, by volume)
Hydrogen Chloride	5	ppm (dry, by volume)
Mercury	10	$\mu g/Nm^3$ (dry)

Results and Discussion

Table 2 contains the data for three different catalyst types, examined under PRB simulated flue gas, which are intended to provide a comparison of the three catalysts.

Table 2. Comparison of mercury oxidation for three catalyst types in simulated PRB flue gas.

Catalyst	Hg^O (ug/m^3)	Hg^T (ug/m3)	Oxidized Hg (ug/m3)	Oxidized Hg/ Hg^T	Oxidized Hg/ average blank Hg^T	Date
blank @ 650°	8066	10898	2832	26.0%	27.1%	8/2/2005
blank @ 750°	7193	9844	2650	26.9%	25.4%	7/18/2005
blank @ 750°	8532	10132	1600	15.8%	15.3%	8/6/2005
blank @ 750°	7955	10911	2956	27.1%	28.3%	8/12/2005
average blank	7936	10446	2510	24.0%	24.0%	-
Honeycomb @ 650°F	10313	10937	624	5.7%	6.0%	8/2/2005
Honeycomb @ 700°F	9646	10502	857	8.2%	8.2%	8/4/2005
Honeycomb @ 750°F	10118	10506	388	3.7%	3.7%	8/5/2005
Hybrid @ 650°F	5724	7606	1882	24.7%	18.0%	8/8/2005
Hybrid @ 700°F	8620	9445	825	8.7%	7.9%	8/7/2005
Hybrid @ 750°F	10026	10450	424	4.1%	4.1%	8/6/2005
Plate @ 650°F	4674	7088	2414	34.1%	23.1%	8/12/2005
Plate @ 700°F	8228	11574	3346	28.9%	32.0%	8/11/2005
Plate @ 750°F	10807	11436	629	5.5%	6.0%	8/12/2005
Honeycomb @ 750°F w/o SO_2	12286	12800	515	4.0%	4.9%	7/18/2005
Honeycomb @ 750°F w/o NH_3	3942	8522	4581	53.7%	43.8%	7/14/2005
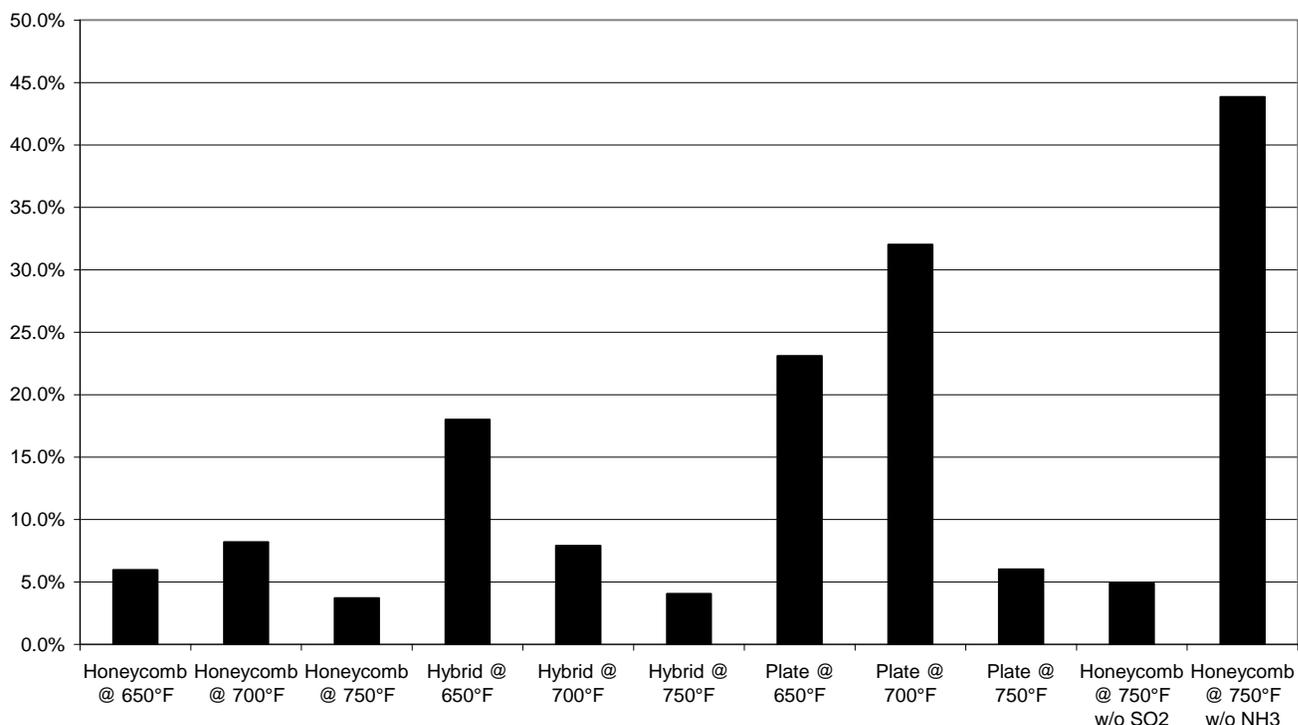
Figure 5. Mercury oxidation comparison of three catalyst types in PRB simulated flue gas.

Averages were taken over two hours when a catalyst was in the reactor and an hour for the blanks. Three chloride samples were taken by bubbling gas through a carbonate bicarbonate impinger in an ice bath. Ion chromatography was used to determine the chloride mass in each sample. The three samples were 5.9, 4.3, and 5.1 ppm. Because of this low precision and accuracy (2 ppm was the target), future tests will use a mass flow controller instead of a rotameter, in an effort to more precisely meter the injection of HCl into the system. SO_3 samples were taken using controlled condensation. All measurements of the plate and hybrid catalysts yielded approximately 15 ppm of SO_3; however, only at 750°F did the honeycomb catalyst show any appreciable conversion of SO_2, which yielded only 5 ppm SO_3.

For the given condition, the plate catalyst oxidized the most mercury, followed closely by the hybrid catalyst. Interestingly, the particular honeycomb catalyst sample tested yielded both the lowest mercury oxidation and lowest SO_2/SO_3 conversion. The most effective temperature for mercury oxidation across the plate and hybrid catalysts was found to be at 700°F. All catalysts showed the lowest oxidation at 750°F.

As mentioned in earlier reports, ammonia inhibits mercury oxidation across SCR catalysts. Additional evidence has been gathered on this mechanism. The honeycomb catalyst at 750° F oxidized 43.8% of the mercury without ammonia and only 3.7% with ammonia. Also, the same test was done with ammonia but without SO_2; the mercury oxidation was 4.9%. The Hg-oxidation difference with an without SO2 present (4.9% - 3.7%) was within the uncertainty of the data. The average mercury oxidation with a blank reactor with no ammonia was 24.0%, which means that, in the presence of low chlorine concentrations, ammonia inhibited oxidation more than a blank reactor without ammonia. Because of the formation of sulfates, it is

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impractical to use the blank reactor with ammonia and SO_2; however, for future tests, a blank will be run with ammonia and without SO_2.
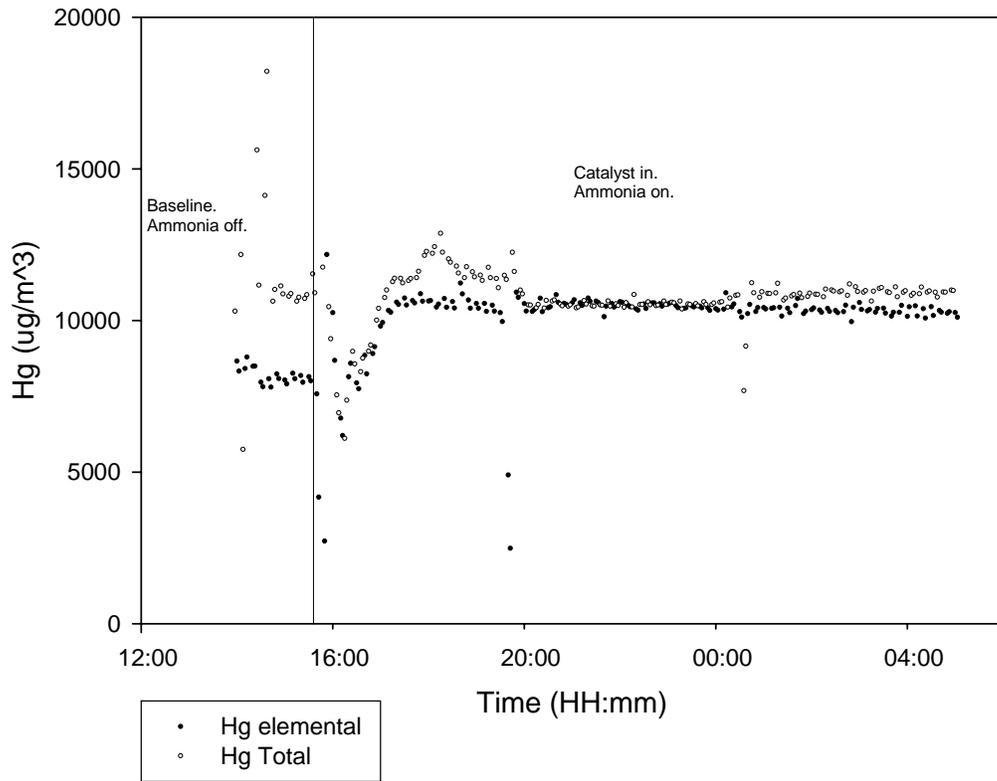
Conclusions

Preliminary tests with high chlorine (250 ppm), high sulfur (2500 ppm SO_2) flue gas indicate that oxidation is 80% and above with a blank reactor. This oxidation is too high to accurately compare the three catalysts. Additional preliminary tests with a blank reactor were done by increasing the HCl concentration incrementally from 0 to 250 ppm. Although equipment failure prevented the test from being completed, the preliminary test showed a somewhat linear relationship with mercury oxidation and HCl concentration. This preliminary result, combined with data showing the relatively minute contribution of SO_2, suggests that a better test may come from concentrating more on varying HCl concentration than temperature and other flue gas constituents. This will be done by setting the reactor to 700°F, setting SO_2 to a medium level (~1000 ppm) with the other constituents at the PRB levels, and monitoring mercury with HCl levels of 25, 50, and 100 ppm with each catalyst. Because the temperature will not vary, there would be fewer leaks to cause delays in testing. At the completion of these tests, further tests would be done to quantify repeatability and the relationship of temperature and SO_2 to mercury oxidation and SO_3 formation. At low chlorine levels (i.e., PRB type flue gas), the plate and hybrid catalyst samples oxidized more mercury than the honeycomb catalyst sample. However, the honeycomb-type catalyst sample converted less SO_2 to SO_3.
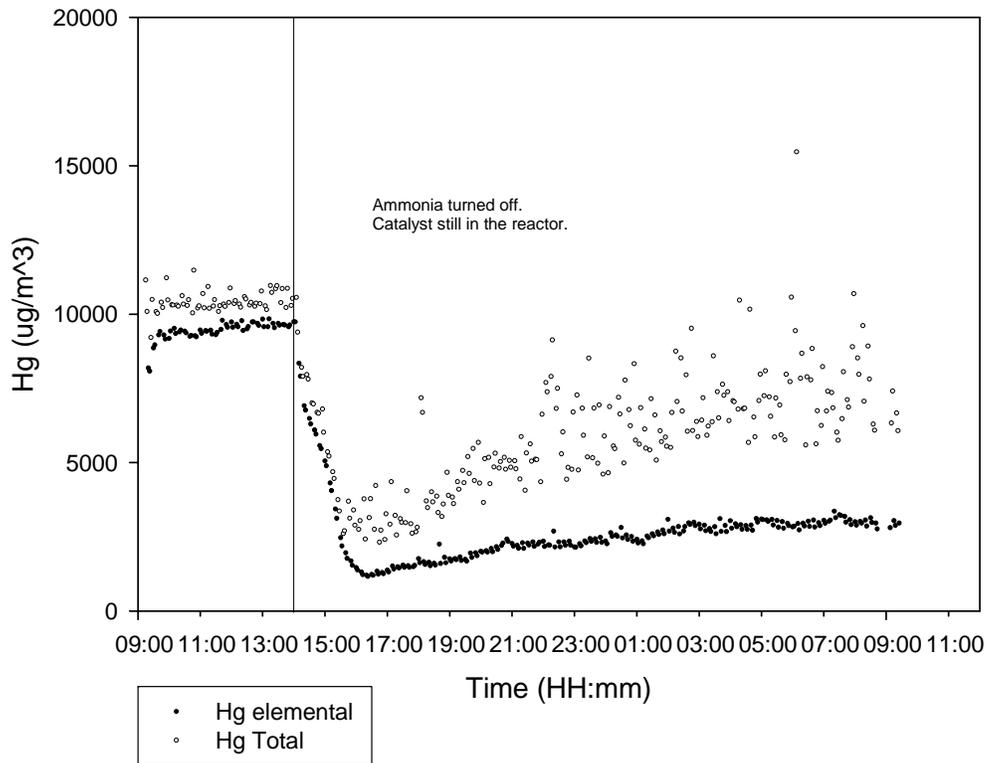
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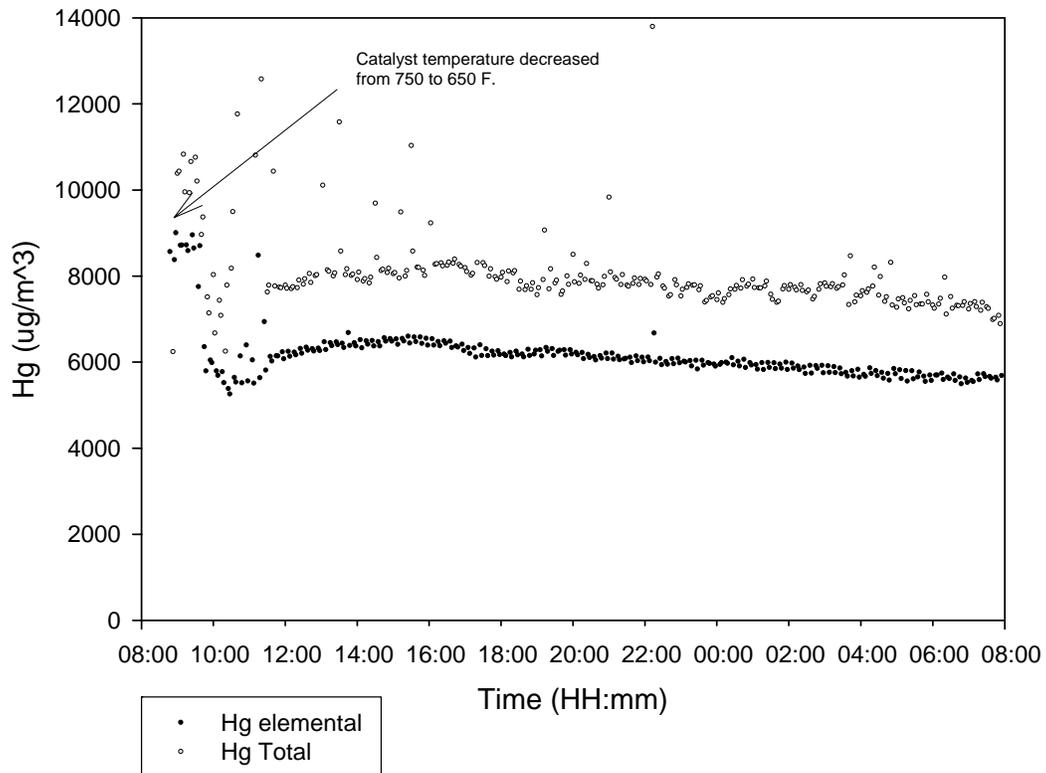
Appendix

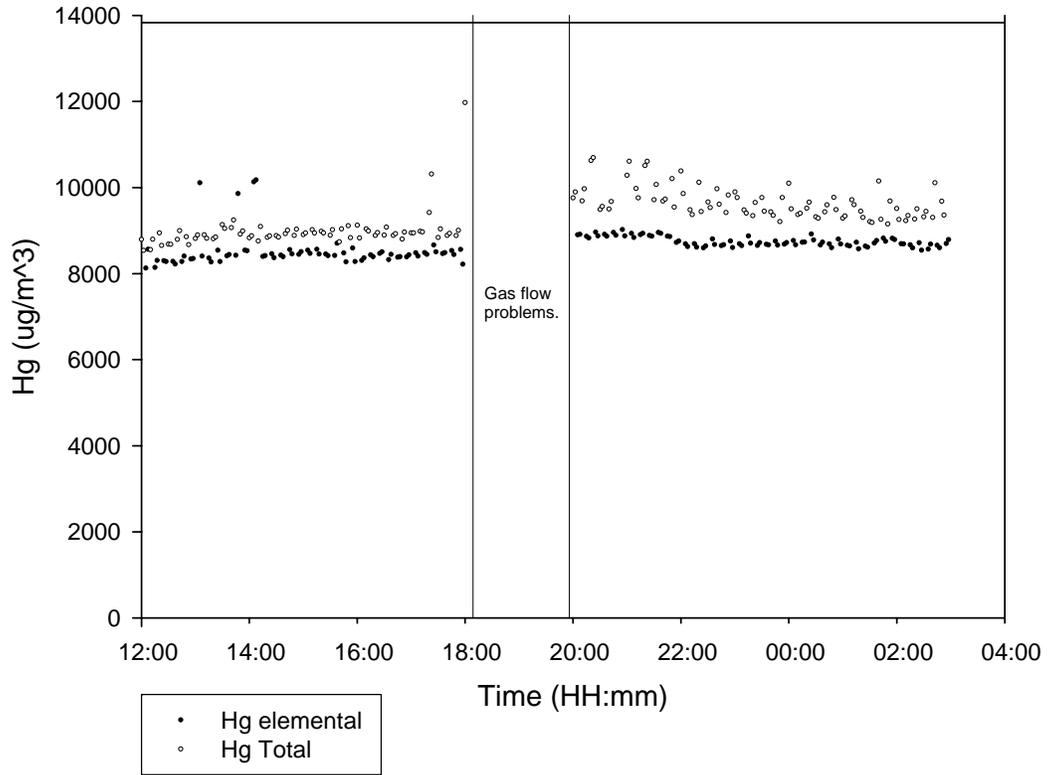**Figure A1.** Honeycomb – PRB – 650°F.

Figure A2. Honeycomb – PRB –700°F.

Data on this chart begins with ammonia being turn on and
the catalyst temperature increased from 700 to 750 F.

- • Hg elemental
- ∘ Hg Total
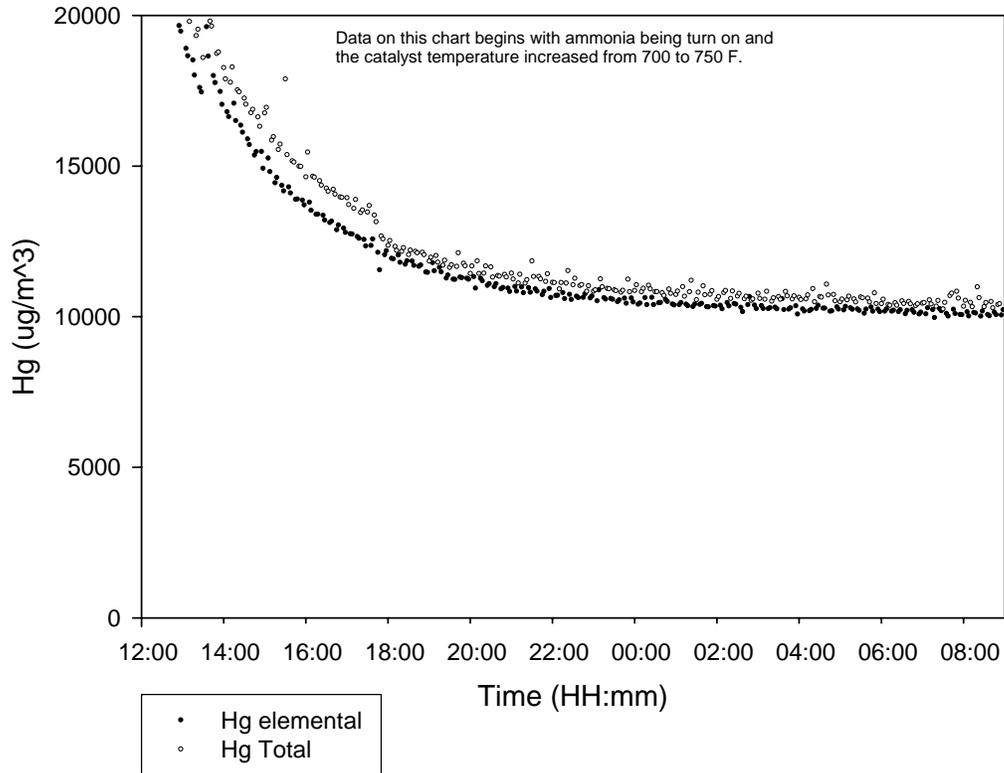
Figure A3. Honeycomb – PRB – 750°F.

Catalyst temperature decreased
from 750 to 650 F.
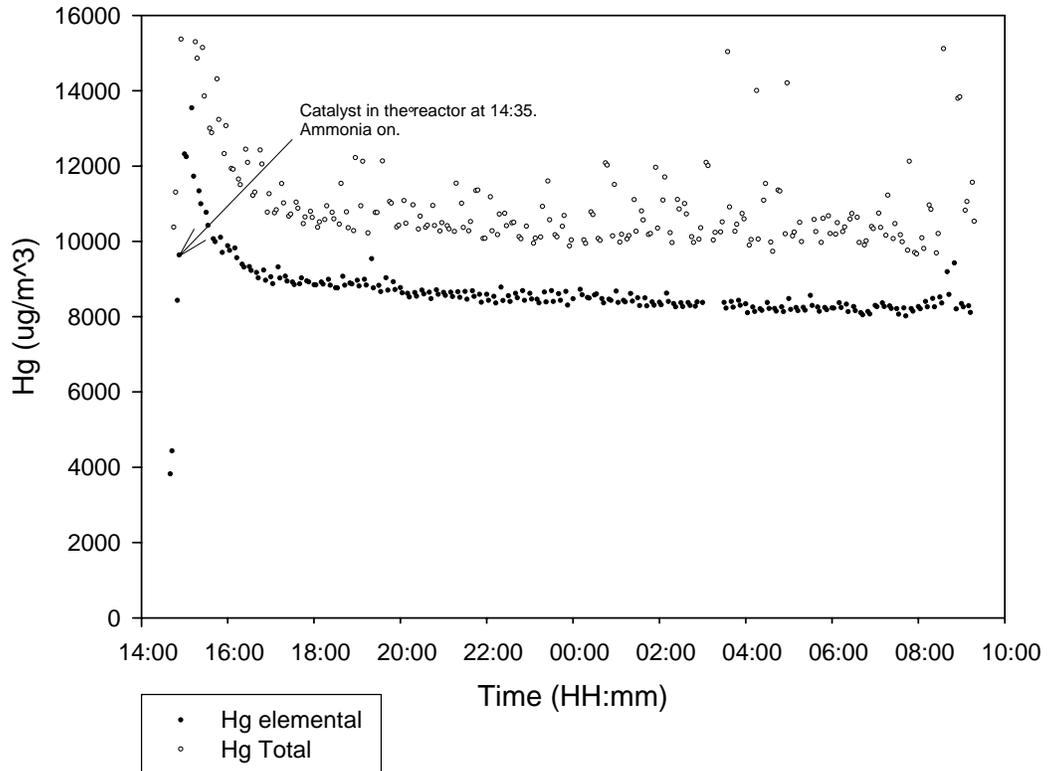
- • Hg elemental
- ∘ Hg Total

Figure A4. Hybrid – PRB – 650°F.

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Figure A5. Hybrid – PRB – 700°F.
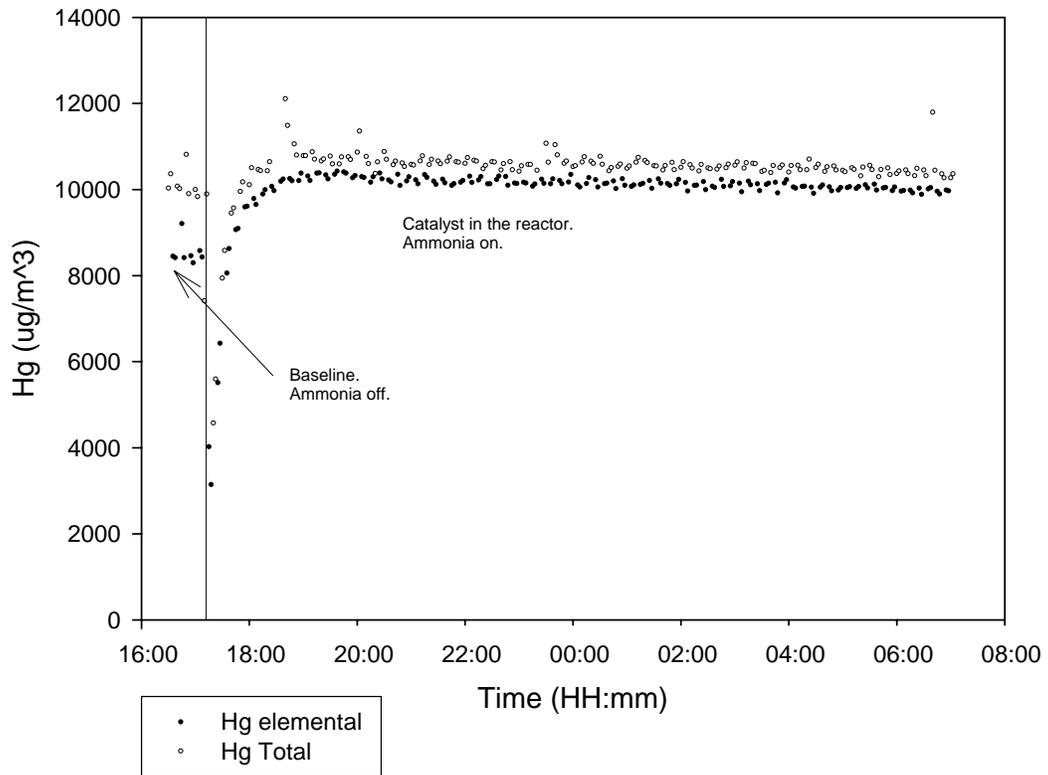
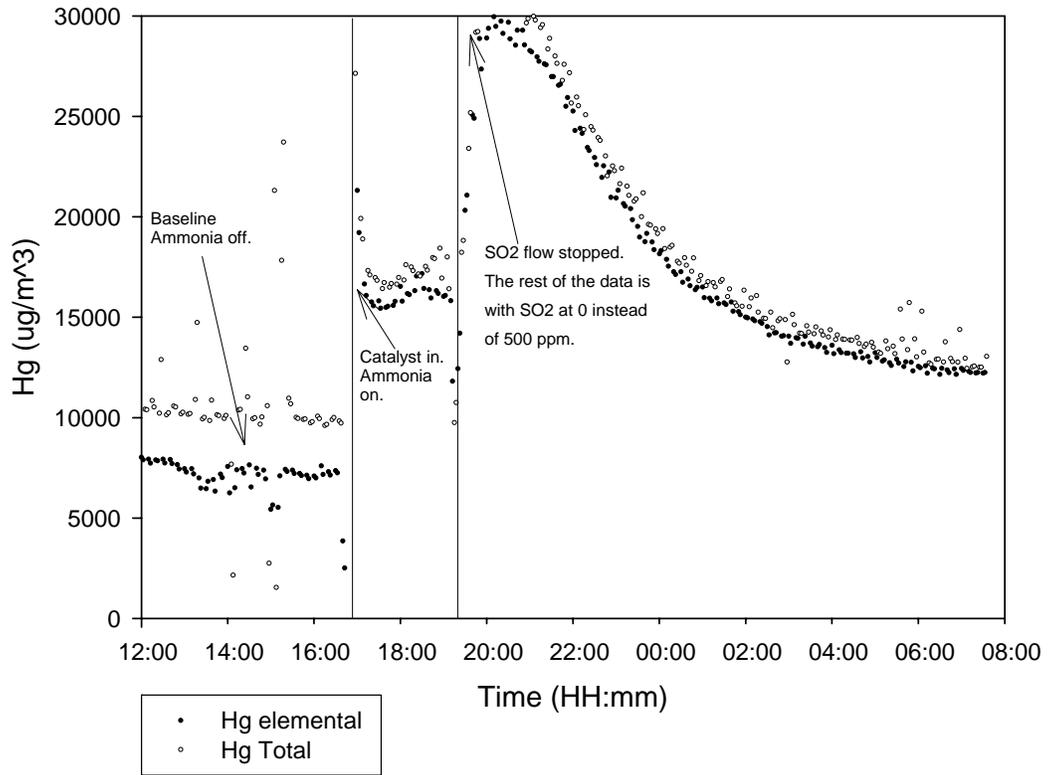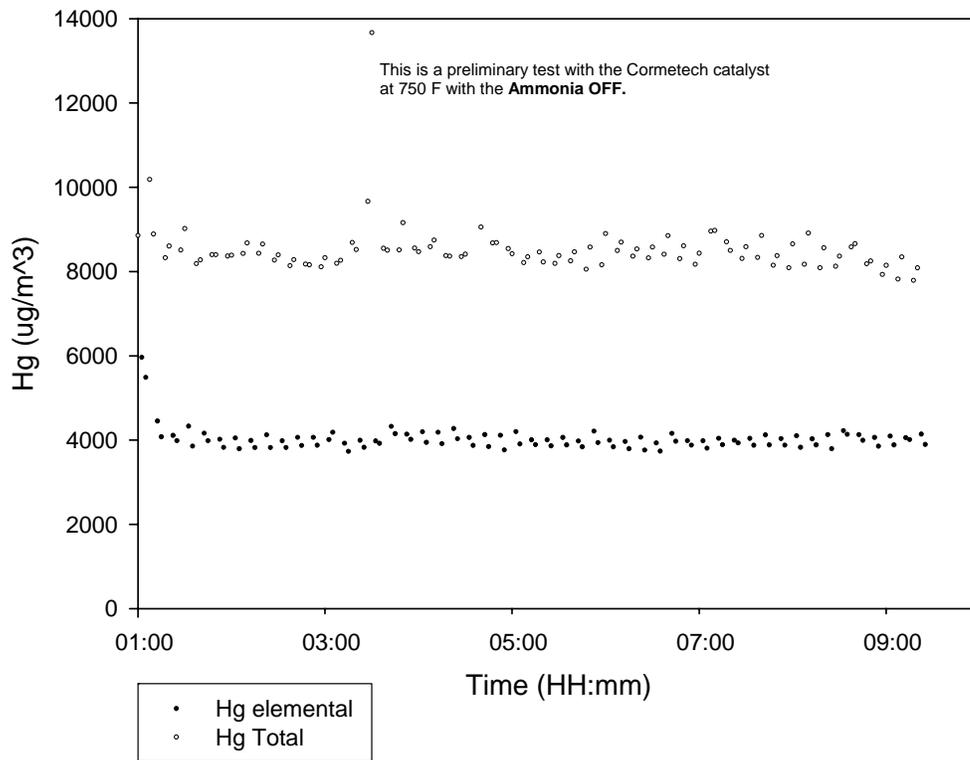**Figure A6.** Hybrid – PRB – 750°F.
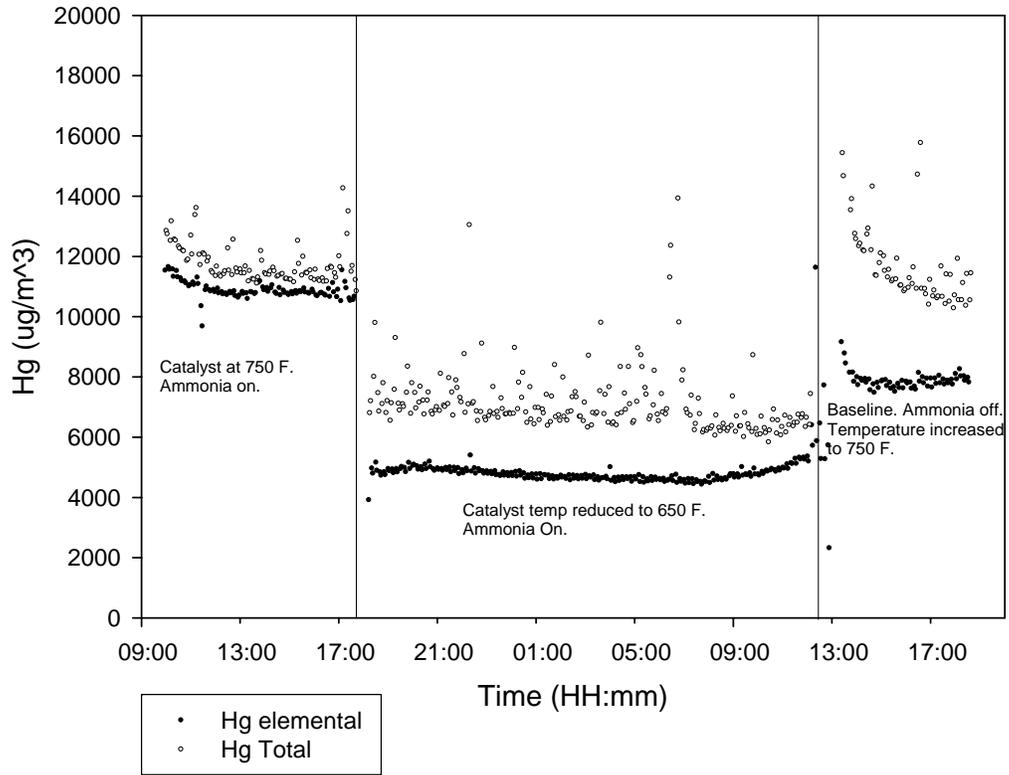
Figure A7. Plate – PRB – 650 & 750°F.

Figure A8. Plate – PRB – 700°F.

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Figure A9. Honeycomb – PRB – SO$_2$ off - 750°F.

Figure A10. Honeycomb – PRB – ammonia - 750°F.

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