



*Jason D. Laumb
Principal Investigator*

DEVELOPING SCR TECHNOLOGY OPTIONS FOR MERCURY OXIDATION IN WESTERN FUELS

Key Personnel: Mike Holmes (EERC), Steve Benson (EERC), Kevin Galbreath (EERC), Ye Zhuang (EERC), Ed Olson (EERC), Jason Laumb (EERC), Flemming Hanson (Haldor Topsoe)

Project Description

The project evaluated the ability of selective catalytic reduction (SCR) catalysts to oxidize mercury. The EERC study included both currently used SCR catalysts and new SCR catalysts formulated to enhance mercury oxidation, as well as the use of additives to enhance oxidation. The first catalyst tested was an existing formulation that Haldor Topsoe currently manufactures. A second set of tests was conducted on several new formulations developed in cooperation with Haldor Topsoe. The catalyst was tested in flue gas compositions similar to what is found in plants burning Powder River Basin (PRB) and lignite coals. The use of oxidation additives to promote the formation of oxidized mercury to levels of those seen for eastern coals was also a primary emphasis.

Goal

The primary goal is to demonstrate that high concentrations of elemental mercury in certain flue gases can be catalytically oxidized to yield greater than 85% oxidized mercury. This would allow for removal in existing and future scrubbers and enhance the capture of mercury on low-cost sorbents for unscrubbed systems. Specific objectives include the following:

- Identify, the primary component(s) in SCR catalysts that contribute to mercury oxidation
- Quantify the effects of various oxidants on mercury oxidation across SCR catalysts
- Evaluate the effects of temperature (650° and 350°F)
- Evaluate the effects of ammonia

Rationale

There is an increasing recognition of the need for mercury control technologies specifically targeted toward plants burning western U.S. coals which emit predominantly elemental mercury. Laboratory and field tests indicate that western coals pose unique challenges in meeting future mercury control requirements. Recent field data have shown that while significant oxidation of elemental mercury occurs across SCR systems for certain applications, there are also applications where no conversion is measured (1, 2). In four utility tests (three sites) with eastern bituminous coals, the elemental mercury

levels averaged 63% upstream of the SCR and 26% downstream. For a single utility site burning PRB coal, the elemental mercury went from 92% to 82% across the SCR. These data indicate that the mercury in low-rank western coals may be more difficult to oxidize, and one of the likely causes is low chlorine levels in these coals.

Roughly two-thirds of the Texas and North Dakota lignite-fired generation capacity is currently equipped with either wet or dry scrubbers. In addition, enactment of the Clear Skies Act or other multipollutant bills would increase the likelihood of new SCR and scrubber installations. For these units, the best-case scenario is development of a cost-effective mercury oxidation technology to allow removal in the scrubbers. Additionally, for plants burning low-sulfur PRB coals, increasing the level of mercury oxidation will enhance the effectiveness of sorbent injection systems.

Approach

The work was completed in two Tasks. Tasks 1 and 2 were completed in the EERC's mercury laboratory. A standard concentration of 15 $\mu\text{g}/\text{Nm}^3$ of elemental mercury was used in the flue gas. In addition to Tasks 1 and 2, blank testing was performed on the reactor with no catalysts to determine any influence the reactor may have on mercury oxidation.

Task 1 – Evaluation of Flue Gas Additives and Temperature

Task 1 attempted to quantify the effects of several variables on the performance of a typical commercially available SCR catalyst in oxidizing elemental mercury. A baseline flue gas composition which simulates that from a low-rank western coal was used, and the bench-scale system was modified to enable catalyst testing. The flue gas composition was fairly typical of that from most western coals in terms of low HCl and SO₂ concentrations. The most critical variables were the type and quantity of mercury oxidants. Candidate oxidants for addition to the gas stream include HCl, other chlorine species, other halogen species, and acid gases. Another important variable is the flue gas temperature at the catalyst. Tests were performed at both 350° and 650°F to determine the effectiveness of the catalyst at a lower temperature where the equilibrium further favors the oxidized forms of mercury. Other researchers have performed limited experiments that show improved oxidation at lower temperatures. In addition, the effect of ammonia was evaluated at 650°F to determine if there are any effects as reported by others (1-7). The impact of ammonia reported by others has been mixed, varying from a negative effect to no effect. Limited testing with ammonia addition was performed to identify any effects with the baseline SCR catalyst.

Table 1 below contains the test plan for the flue gas concentrations tested under this task. An inlet mercury concentration of 12 $\mu\text{g}/\text{Nm}^3$ was used. The catalyst was a standard catalyst provided by Haldor Topsoe. The baseline flue gas simulated a utility burning a low-rank fuel. Components such as HCl, NO, and SO₃ were varied as noted in Table 1.

The testing was completed on an existing bench-scale laboratory with the addition of an SCR chamber. The reactor chamber is approximately 1.5 in. square and 14 in. long. The reactor was housed in an oven that was maintained at the appropriate temperature as describe in the work plan. Enough tubing was coiled in the oven to ensure that gases were at the appropriate temperature prior to entering the reactor. For tests when the SCR reactor is bypassed, the flue gas still passed through the oven and was heated to the appropriate temperature. The level of oxidized and elemental mercury was monitored at the

Table 1. Test Plan for Task 1

Baseline Test	
Velocity	5 m/s
O ₂	6%
CO ₂	12%
H ₂ O	15%
NO	Variable
HCl	None
NO ₂	6 ppm
Hg ⁰	12 µg/Nm ³
SO ₃	Variable
NH ₃	Variable
N ₂	Balance
Temperature	343°C (650°F)
Catalyst	Baseline

inlet and the outlet of the SCR chamber. The catalyst was allowed to condition at temperature for a period of 1 hour prior to feeding Hg in the system. Three additional tests were performed upon completion of the matrix in Table 1. The conditions for the additional tests were chosen based on the results of the first runs.

Task 2 – Development of SCR Catalyst for Mercury Oxidation

Task 2 attempted to identify improved catalyst formulations for oxidizing elemental mercury. Haldor Topsoe developed and supplied different catalyst formulations and provided cofunding for its testing under this task. Three new catalyst formulations were tested. Table 2 below contains the test plan for three catalyst formulations under this task. The three formulations were those other than the standard SCR catalyst offered by Haldor Topsoe. The standard catalyst was tested as a baseline under Task 1 and was in addition to the three tests planned below.

Table 2. Test Plan for Task 2

	Topsoe Test 1	Topsoe Test 2	Topsoe Test 3
Velocity	5 m/s	5 m/s	5 m/s
O ₂	6%	6%	6%
CO ₂	12%	12%	12%
H ₂ O	15%	15%	15%
NO	Variable	Variable	Variable
HCl	Variable	Variable	Variable
NO ₂	6 ppm	6 ppm	6 ppm
Hg ⁰	12 µg/Nm ³	12 µg/Nm ³	12 µg/Nm ³
SO ₃	Variable	Variable	Variable
NH ₃	Variable	Variable	Variable
N ₂	Balance	Balance	Balance
Temperature	Variable	Variable	Variable
Catalyst	Topsoe X	Topsoe Y	Topsoe Z

The flue gas concentrations were intended to mimic those of a low-rank fuel. Approximately 12 $\mu\text{g}/\text{Nm}^3$ of elemental mercury was added to the bench-scale system. Small amounts of ammonia were added to mimic a full-scale SCR system. The amount of elemental and oxidized mercury before and after the SCR catalyst chamber was measured. The catalyst was allowed to condition at temperature for a period of 1 hour prior to feeding Hg in the system.

Additional Work

The EERC also tested a proprietary additive denoted as Sorbent Enhancement Additive (SEA) 2. This is a proprietary flue gas additive that may enhance the conversion of elemental mercury to an oxidized state. The test conditions used for Tasks 1 and 2 were used for the testing of this additive.

Progress

The results of the blank testing are shown in Table 3. The data indicate that very little to no mercury was oxidized without the presence of catalyst for all test conditions. A small increase in mercury oxidation was observed when increasing HCl concentrations without increasing SO_3 .

The results of Task 1 are shown in Table 4 below. In general, better results were found when using Cl_2 as a catalyst as opposed to HCl. The best results were obtained from Test 4, where chlorine gas was used in conjunction with ammonia in the absence of SO_3 . From the test matrix below, it is impossible to tell exactly which component(s) had the greatest effect on the oxidation of mercury. Additional testing would be needed to verify the results.

The results of Task 2 are shown in Table 5 below. Overall, Catalyst Z performed better than the other two catalysts. Catalyst X performed worse than the baseline catalyst. Catalysts Y and Z performed differently with the varying flue gas conditions. Both Y and Z favored higher HCl concentrations, but Catalyst Z performed best with high concentrations of NO_x and ammonia. Catalyst Y favored lower concentrations of NO_x and ammonia. As with the previous test, follow-on runs are needed to determine exactly which input variables are having the greatest effects.

Table 3. Blank Testing with No Additives in the SCR Reactor

Test	O_2 , %	CO_2 , %	H_2O , %	NO_2 , ppm	NO , ppm	HCl, ppm	SO_2 , ppm	SO_3 , ppm	% Elemental Hg
1	0	0.12	0.15	0	0	0	0	0	102
2	0	0.12	0.15	6	120	1	600	12	101
3	0	0.12	0.15	6	120	1	600	0	100
4	0	0.12	0.15	6	600	1	600	0	103
5	0	0.12	0.15	6	120	10	600	0	97
6	0	0.12	0.15	6	300	10	600	0	95
7	0	0.12	0.15	6	600	10	600	0	93
8	0	0.12	0.15	6	120	10	600	12	98
9	0	0.12	0.15	0	0	0	0	0	98

Table 4. Task 1 Test Results Utilizing Standard Catalysts

(Constant: O ₂ : 6%, CO ₂ : 12%, H ₂ O: 15%, NO ₂ : 6 ppm, SO ₂ : 600 ppm, Hg ⁰ :12 µg/m ³)								
Test	Conditions							Results
	HCl, ppm	Cl ₂ , ppm	SO ₃ , ppm	NO, ppm	NH ₃ , ppm	~NO _x , ppm	Temp °C (°F)	% Elemental Hg
1		1	12	120	108	14	343 (650)	85
2		1	0	120	108	24	343 (650)	84
3		10	0	120	108	18	343 (650)	73
4		10	0	300	270	27	343 (650)	65
5		10	12	300	0	*	343 (650)	94
6		10	12	120	0	128	343 (650)	83
7		10	12	120	0	128	177 (350)	93
8	1		12	120	108	20	343 (650)	96
9	1		0	120	108	20	343 (650)	96
10	1		0	600	540	*	343 (650)	100
11	1		0	120	0	128	343 (650)	100
12	10		0	120	108	25	343 (650)	93
13	10		0	300	270	25	343 (650)	89
14	10		0	600	540	*	343 (650)	86
15	10		12	120	108	20	343 (650)	99
16	10		12	120	0	121	343 (650)	100
17	10		12	120	0	121	343 (650)	96

* High variability.

Table 5. Task 2 Test Results Utilizing Proprietary Topsoe Catalysts

(Constant: O ₂ : 6%, CO ₂ : 12%, H ₂ O: 15%, NO ₂ : 6 ppm, SO ₂ : 600 ppm, Hg ⁰ : 12 µg/m ³)								
Test	Conditions					% Elemental Hg		
	HCl, ppm	SO ₃ , ppm	NO, ppm	NH ₃ , ppm	Temp., °C (°F)	Cat. X	Cat. Y	Cat. Z
1	1	12	120	108	343 (650)	90%	99%	97%
2	10	0	120	108	343 (650)	92%	75%	82%
3	10	12	120	108	343 (650)	*	73%	78%
4	10	0	600	540	343 (650)	93%	86%	62%
5	10	0	120	0	343 (650)	96%	90%	*
6	10	0	120	0	177 (350)	100%	92%	*

* Steady state not achieved in time allotted.

In addition to the additives tested in Tasks 1 and 2, the EERC also tested an additional proprietary additive denoted as SEA2. The results of this testing are shown in Table 6 below. The results of the test indicate elemental mercury concentration was 43% at the SCR outlet. This result is an improvement over the other catalysts tested in this study. There was some question with regard to the integrity of the data because it contained multiple mercury spikes. One theory for the occurrence of the spikes is that the catalyst is desorbing mercury as it nears the continuous mercury monitor (CMM). Despite showing some promise, more testing on this catalyst will be needed to determine if it is truly more effective and to determine the mechanism for the mercury spikes.

Table 6. Test Results Utilizing Catalyst SEA2

(Constant: O₂: 6 %, CO₂: 12 %, H₂O: 15%, NO₂: 6 ppm, SO₂: 600 ppm, Hg⁰: 12 µg/m³)

Test	Conditions					% Elemental Mercury
	HCl, ppm	SO ₃ , ppm	NO, ppm	NH ₃ , ppm	Temp., °C (°F)	
1	1	0	120	0	343 (650)	43%

Conclusions

Catalyst Z performed better than all other catalysts in this study. Catalyst Z performed best with high levels of ammonia and HCl. Catalyst Y performed better under different flue gas conditions than catalyst Z. Catalyst Y preferred lower levels of ammonia than Catalyst Z, but did not perform well in the absence of ammonia. Catalyst X performed worse than the baseline catalyst.

Increasing the HCl concentration had positive results in all cases except for Catalyst X. Decreasing temperature did not have a positive effect on catalyst performance. The addition of ammonia shows some promise for mercury oxidation, and should be tested further. SEA2 additive is showing some promise, but more work will be needed to fully quantify the effects of this catalyst.

Based on these results, it is recommended that additional studies be performed on Catalysts Y, Z, and SEA2. Ideally, a statistically designed experiment should be run with replication for each catalyst. The results of this test indicate HCl and temperature should be kept at the high levels, which would reduce the cost of running a designed experiment for follow-on tests.

Status

The testing and reporting are complete.

Quality Assurance/Quality Control (QA/QC)

The following procedures will be used to ensure data quality:

- Sampling and analytical analysis protocols will be validated by comparing test data with other data generated using standard protocols in place at the EERC.
- The type and quantity of QA samples will include calibration of the CMMs, replicate tests (minimum of three), and a blank at the beginning at each day.
- The QA/QC data results will then be compared with data quality indicators to qualitatively determine the validity of the data in terms of precision and accuracy. Only when mass balances are ±30% will the data be considered valid.

Activities within this project are focused on advancing the knowledge of and options for mercury control via oxidation in a SCR catalyst system. The quality objective of this project is to provide appropriate data that can be examined to test the working hypothesis. These results will be used to determine whether mercury can be effectively oxidized by improved formulations of SCR catalyst under

optimum conditions of oxidant concentration(s) and temperature to serve as the basis for enhancing mercury control technologies for western U.S. coals.

The system is calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial which is held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is measured using vapor pressure calculations. Typically, the calibration of the unit has proven stable over a 24-hr period.

Potential Users/Technology Transfer

Potential users of this technology will be any utility that wishes to use catalyst to enhance mercury oxidation and capture, especially utilities burning western fuels (lignite and PRB) where there is a low concentration of chlorine and, therefore, very little oxidized mercury. Oxidized mercury can more easily be captured in existing pollution control devices.

References

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