FUNDAMENTAL STUDY OF THE IMPACT OF SCR ON MERCURY SPECIATION

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Project Description

Previous testing conducted by the Energy & Environmental Research Center (EERC) to evaluate the impact of selective catalytic reduction (SCR) on mercury speciation indicated that the impact is coal-specific. To investigate the role that SO_2/SO_3 and HCl/Cl_2 concentrations in the coal play, bench-scale tests using a fixed-bed system were conducted to help determine the effects of these gases. A full-factorial design was used to evaluate the independent variables, including the reactor (none, SCR), presence of acid gases (HCl and SO_2/SO_3), fly ash type, and residence time. The presence of ammonia (NH_3) depended on reactor mode.

Goal

The goal of this project was to determine the factors that have the potential to alter mercury speciation when SCR technologies are used. The specific objective was to determine the effects of the different variables on mercury speciation, including flue gas chemistry, fly ash type, and residence time.

Rationale

Many utilities, in anticipation of pending regulations impacting air emissions and to help achieve ozone attainment, are planning to install SCR reactors. Plants equipped with SCR units achieve lower nitrogen oxide (NO_x) emissions by reducing NO_x to N_2 and H_2O in the presence of a catalyst. Generally, NH_3 is the reducing gas, and the system is operated at a temperature of 650°–700°F. Bench-, pilot-, and full-scale testing by the EERC and others have shown that SCR catalysts promote the formation of oxidized mercury (Hg^{2+}) and particulate-bound mercury under some conditions [1, 2]. Therefore, SCRs have the potential to improve mercury removal by promoting the formation of Hg^{2+} and/or particulate-bound mercury formation rather than elemental mercury (Hg^0).

Approach

The variables were carefully chosen for this testing and are considered to be the most important factors in the oxidation of mercury by an SCR reactor. The testing was conducted using a full-factorial design with the following four variables:

- Fly ash type, either an ash generated firing a bituminous or subbituminous coal
- Residence time, either baseline or double the baseline
- With and without an SCR reactor
- With and without acid gases, which includes a combination of SO_2, SO_3, and HCl

A bench-scale system (shown in Figure 1) was specifically designed for the project. Simulated flue gas was used in known concentrations, thereby eliminating the possibility of other influences on the tests. The concentrations of the gases used to generate the simulated flue gas are shown in Table 1.

The temperature, 650°F (343°C), and gas flow rate to the reactor oven was maintained to simulate normal operations of an SCR. A filter, housed in a heated muff, was used to provide contact for the fly ash and simulated flue gas. A PS Analytical (PSA) mercury semicontinuous emission monitor (Hg SCEM) was used to provide measurements of both Hg^0 and total mercury, thereby allowing measurement of Hg^{2+} by difference. For all tests, a known amount of 100% Hg^0 was added to the system prior to the reaction chamber (either SCR or empty chamber), and the amount of Hg^0 was measured at the outlet of the filter, thereby providing the amount of mercury oxidation that occurred as a result of the test variables.

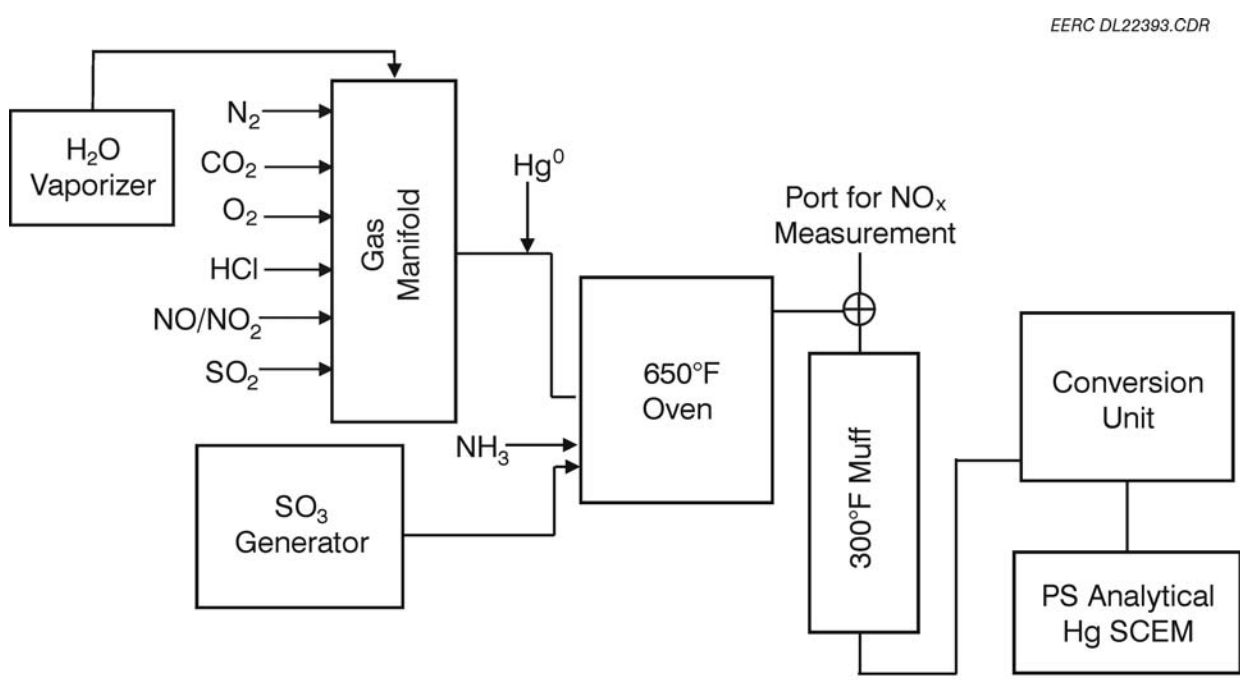

Figure 1. Schematic of the Bench-Scale SCR System

Table 1. Gas Concentrations Used for Simulated Flue Gas

Baseline Gases	
CO_2	10%
O_2	6%
NH_3	550 ppm with SCR
H_2O(v)	8%
Hg^0	13.3 μg/m^3
N_2	Balance
Acid Gases	
SO_2/SO_3	2000/50 ppm
HCl	50 ppm
NO/NO_2	600/18.5 ppm

Progress

Testing has been completed, with results shown in Table 2 and a full-factorial analysis shown in Table 3. The statistic analyses clearly show that the acid gases and the presence of SCR are statistically significant with a two-way interaction between them. When there are no acid gases present, the effect of the SCR is minimal. When the acid gases are present with an SCR, there does appear to be a decrease in the fraction of Hg^0. The statistical analysis shows that the overwhelming factor is the presence of acid gases and an SCR catalyst. It is interesting to note that neither fly ash appeared to have any impact on the oxidation. The bituminous fly ash was taken from a plant that generated highly reactive ash. The results also show that, within the confines of the test, there was no observed residence time effect.

Status

Although testing for this project is finished, the results indicate a need for further testing to isolate other factors that may play a role in mercury oxidation. The following are recommendations for further testing:

1. Additional replications should be performed so that a more fine-tuned statistical analysis can be completed.
2. The acid gases should be separated as individual variables.
3. The SCR catalyst should be seasoned (aged) to help prevent adsorption of mercury.

Quality Assurance/Quality Control

The full-factorial analysis allowed individual consideration to be given to each of the four factors thought to relate to mercury oxidation: presence of SCR, fly ash, presence of acid gases, and residence time. The statistical analysis was performed in order to ensure that causal agents were identified correctly.

All gases, with the exception of Hg^0 and SO_3, were provided using gas cylinders and metered using calibrated mass flow controllers or tube cube flowmeters. Hg^0 was generated using a permeation tube

Table 2. Mercury Results for Bench-Scale Tests

Run	Ash	Residence Time	SCR Present	Acid Gases Present	Hg^0, %
1	Subbituminous	1	No	No	97
2	Bituminous	1	No	No	98.7
2*	Bituminous	1	No	No	102.6
3	Subbituminous	2	No	No	95.1
4	Bituminous	2	No	No	84
4*	Bituminous	2	No	No	90.2
5	Subbituminous	1	Yes	No	104.7
6	Bituminous	1	Yes	No	80.3
7	Subbituminous	2	Yes	No	101.2
8	Bituminous	2	Yes	No	100
9	Subbituminous	1	No	Yes	81.3
10	Bituminous	1	No	Yes	72.4
10*	Bituminous	1	No	Yes	72.6
11	Subbituminous	2	No	Yes	78.5
12	Bituminous	2	No	Yes	60.5
13	Subbituminous	1	Yes	Yes	24.1
14	Bituminous	1	Yes	Yes	22.7
15	Subbituminous	2	Yes	Yes	41.8
16	Bituminous	2	Yes	Yes	47.5

* Indicates replicate tests.

Table 3. Statistical Analysis of Results

Variable	t(effect)
X1 (ash type)	−0.723
X2 (residence time)	0.39
X3 (SCR reactor)	**−2.074***
X4 (acid gases)	**−4.646***
X1X2	0.132
X1X3	0.136
X1X4	0.103
X2X3	1.225
X2X4	0.369
X3X4	**−2.247***
X1X2X3	0.706
X1X2X4	−0.188
X1X3X4	0.722
X2X3X4	0.354
X1X2X3X4	−1.630

* Statistically significant compared to the t(stat) of 1.638.

maintained at a constant temperature. To determine the rate of mercury generated from the permeation tube and to collect mercury speciation data, a PSA Hg SCEM was used. For these tests, only Hg^0 was added (no Hg^{2+}). SO_3 was generated by passing air and SO_2 over a heated catalyst. The rate was determined by measuring the SO_2 flow rate into the unit and SO_2 to SO_3 conversion efficiency.

Potential Users/Technology Transfer

Although full-scale tests seem to indicate the usefulness of SCR reactors as multipollutant control devices, there are numerous factors that impact its ability to oxidize mercury. This project isolated factors so that each variable could be statistically examined individually. As pending regulations on mercury emission levels and ambient air are introduced, utilities must be able to make a rational, informed decision as to the efficiencies of commercially available technologies, as well as system modifications that can be used to meet standards. This test shows that the presence of acid gases containing SO_2/SO_3, HCl, and NO/NO_2 were the most statistically relevant, again showing that manipulation of coal chemistry or additives may play a role in enhanced mercury oxidation, especially if coupled with SCR.

References

1. Galbreath, K.C.; Zygarlicke, C.J.; Olson, E.S.; Pavlish, J.H.; Toman, D.L. Evaluating Mercury Transformation Mechanisms in a Laboratory-Scale Combustion System. *The Science of the Total Environment* **2000**, *261* (1–3), 149–155.

2. Gutberlet, H.; Spiesberger, A.; Kastner, F.; Tembrink, J. Mercury in Bituminous Coal Furnaces with Flue Gas Cleaning Plants. *VGB Kraftwerkstechnik* **1992**, *72*, 586–591.