

Effect of Catalyst Age on Mercury Speciation

Data indicate that additional Hg oxidation can be expected if an SCR unit is installed on a unit firing an eastern bituminous coal. A potential concern is “Does the effectiveness of the Hg oxidation potential of SCR decrease with time?” As has been discussed previously, two of the facilities, S2 and S4, were tested in both 2001 and 2002 (both burned eastern bituminous coal). As Figures ES-1 and ES-2 show, there was a decrease in Hg oxidation across the SCR catalyst in 2002 as compared to 2001. However, the decrease in oxidation seen over time is less than that seen from coal variability. Additionally, it is expected that routine replacement of catalyst layers will minimize the effect. Also, mitigating circumstances at each plant prevent a definitive conclusion from being developed. At Site S2, the temperature of the SCR unit was ~10°F cooler due to humidification, and alkali was added upstream of the SCR unit. At both Sites S4 and S2, the coal chloride concentration was highly variable. Although there may be an “effect” of aging as measured across the SCR unit, Hg measurement at the inlet to the particulate control device indicates there was no significant difference at either site. To understand if these results are indicative of a catalyst aging effect, Hg speciation sampling is recommended at these plants for several additional years.

Effect of the SCR on Wet FGD Performance for Mercury Control

The underlying intent of understanding SCR-mediated Hg oxidation is to determine its potential to improve the Hg collection efficiency of existing ESPs, fabric filters and, in particular, FGD systems. In general, wet FGDs remove a large percentage (>90%) of Hg²⁺. However, there has been evidence that some of the captured Hg²⁺ can be reduced in the wet FGD to Hg⁰ [10]. Although the sample set is very small (three facilities) and the wet FGDs tested to date are not representative of the most common FGD design in the United States (forced oxidation system), the data from this project indicate that some of the Hg²⁺ is chemically reduced to Hg⁰ in the wet FGD. This Hg⁰ passes through the FGD and is therefore not captured, resulting in an increase of Hg⁰ across the FGD. For the purposes of this report, this effect is termed reemission. As can be seen in Table ES-4, at all the sampling sites, there is an increase in Hg⁰ across the FGD. Also, the data seem to indicate the operation of the SCR unit ameliorates possible reemission.

Table ES-4
Effect of the SCR on Hg⁰ Concentration Across the Wet FGDs

Site	Year Sampled	FGD Inlet Hg ⁰ Conc., $\mu\text{g}/\text{Nm}^3$	FGD Outlet Hg ⁰ Conc., $\mu\text{g}/\text{Nm}^3$	Hg ⁰ Increase, ^a $\mu\text{g}/\text{Nm}^3$	Total Hg Removal, %
<i>With SCR</i>					
S2	2001	0.4 ^b	0.9	0.5	89
S2	2002	0.3	1.3	1.0	84
S4	2001	0.5	0.8	0.3	90
S4	2002	1.0	1.3	0.3	91
S5	2002	0.7	1.0	0.3	91
<i>Without SCR</i>					
S2	2001	3.4 ²	5.0	1.6	51
S4	2001	5.6	7.1	1.5	46
S4	2002	5.7	8.0	2.3	44
S5	2002	4.7	6.1	1.4	51

^a Defined as (FGD outlet Hg⁰ conc. – FGD inlet Hg⁰ conc.).

^b For 2001 Site S2 data, the ESP inlet data were used because the FGD inlet Hg concentration values appear to be clear outliers.

Summary

The primary conclusions based on the test results are:

- For plants firing eastern bituminous coals, Hg⁰ can be oxidized across the SCR catalysts. The effect that SCR has on Hg speciation (i.e., extent of additional oxidation that occurs) may be dependent upon the coal characteristics and catalyst properties. The percentage increase of Hg²⁺ at the SCR outlet ranged from 10% at Site S3 to 71% at Site S4.
- At both sites where sampling was done in 2001 and 2002, there appeared to be a decrease in Hg oxidation across the SCR catalyst with time. However, at both facilities, the decrease was minimal, and other possible explanations related to changes in the plant's operation might explain the decrease. These changes do not allow a definitive conclusion to be reached concerning the effect of catalyst age (an additional ozone season) on SCR/Hg oxidation. It is important to note that the measured Hg oxidation at the inlet to the particulate control device was the same (within the variability of the data) for both years.
- Based on the limited data at three plants (five total data sets), SCR operation may reduce the extent of reemission across the wet FGDs. For the tests with SCR in service, the increase appears to be very small and is generally within the variability of the data. Nevertheless, five data points show an increase in Hg⁰. When SCR is not in service, it appears that the reemission is more pronounced.

Future Test Plans

Based on a review of these test results, several areas will require further investigation. DOE, EPA, and EPRI are planning to conduct additional full-scale, as well as bench- and pilot-scale, studies to address the following:

- The effect of SCR for a PRB pulverized coal application.
- The effect of FGDs on Hg capture, in particular Hg reemission.
- The effect of SCR when PRB-bituminous-blended coal is fired.
- The effect of catalyst age on Hg speciation.

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CONTENTS

1 INTRODUCTION	1-1
1.1 Potential Impacts of SCR on Mercury Speciation	1-1
1.2 Pilot-Scale Screening Tests Conducted at the EERC.....	1-2
1.3 2001 SCR Mercury Field-Sampling Project	1-3
1.4 Project Goals and Objectives	1-5
1.5 Sampling Approach.....	1-5
1.5.1 Mercury Sampling Using the Ontario Hydro Mercury Speciation Method.....	1-5
1.5.2 Mercury Sampling Using Hg SCEMs	1-6
1.5.3 Other Flue Gas Analyses	1-7
1.5.4 Mass Balance.....	1-7
1.5.5 Plant Operation Data	1-7
2 SITE S2	2-1
2.1 Site Description and Configuration	2-1
2.2 Sampling Approach.....	2-2
2.2.1 Flue Gas Sample Streams.....	2-3
2.2.2 Other Sample Streams	2-3
2.3 Process Operating Conditions.....	2-4
2.4 Sampling Results	2-7
2.4.1 OH Flue Gas Mercury Results	2-7
2.4.2 Hg SCEM Results	2-8
2.4.3 Coal Analysis Results.....	2-11
2.4.4 ESP Ash and FGD Mercury Results	2-12
2.4.5 NH ₃ Slip and SO ₃ Flue Gas Results	2-13
2.5 Mercury Mass Balance.....	2-14
2.6 General Observations from S2.....	2-14
3 SITE S4	3-1

3.1	Site Description and Configuration	3-1
3.2	Sampling Approach.....	3-2
3.2.1	Flue Gas Sample Streams.....	3-3
3.2.2	Other Sample Streams	3-3
3.3	Process Operating Conditions.....	3-3
3.4	Sampling Results	3-5
3.4.1	OH Flue Gas Mercury Results.....	3-5
3.4.2	Hg SCEM Results	3-7
3.4.3	Coal Analysis Results.....	3-9
3.4.4	Mercury Collected by the Venturi Scrubber	3-10
3.4.5	NH ₃ Slip and SO ₃ Flue Gas Results for Site S4	3-11
3.5	Mercury Mass Balance.....	3-11
3.6	General Observations from S4.....	3-12
4	SITE S5	4-1
4.1	Site Description and Configuration	4-1
4.2	Sampling Approach.....	4-3
4.2.1	Flue Gas Sample Streams.....	4-3
4.2.2	Other Sample Streams	4-4
4.3	Process Operating Conditions.....	4-4
4.4	Sampling Results	4-9
4.4.1	OH Flue Gas Mercury Results.....	4-9
4.4.2	Hg SCEM Results	4-11
4.4.3	Coal Analysis Results.....	4-14
4.4.4	ESP Ash Mercury Results	4-15
4.4.5	NH ₃ Slip and SO ₃ Flue Gas Results	4-16
4.5	Mercury Mass Balance.....	4-17
4.6	General Observations from S5.....	4-17
5	SITE S6	5-1
5.1	Site Description and Configuration	5-1
5.2	Sampling Approach.....	5-4
5.2.1	Flue Gas Sample Streams.....	5-5
5.2.2	Other Sample Streams	5-5
5.2.3	Process Operating Conditions	5-6

5.3	Sampling Results	5-12
5.3.1	OH Flue Gas Mercury Results	5-12
5.3.2	Hg SCEM Results	5-14
5.3.4	Coal Analysis Results	5-20
5.3.5	ESP Ash Analysis	5-21
5.3.6	NH ₃ Slip and SO ₃ Flue Gas Results	5-21
5.4	Mercury Mass Balance	5-22
5.5	General Observations from S6	5-23
6	DISCUSSION OF OVERALL RESULTS	6-1
6.1	The Change in Mercury Oxidation Across the SCR Catalysts	6-3
6.2	Effect of the SCR on Mercury Oxidation	6-5
6.3	Effect of SCR Catalyst Age on Mercury Speciation	6-6
6.4	SCR/Wet FGD Combination for Mercury Control	6-8
7	CONCLUSIONS	7-1
	Future Test Plans	7-1
8	QUALITY ASSURANCE/QUALITY CONTROL	8-1
8.1	Process Data Evaluation	8-1
8.2	Sampling Quality Control Evaluation	8-2
8.3	Evaluation of Measurement Data Quality	8-3
8.4	OH Method Error Analysis	8-5
9	REFERENCES	9-1
A	SAMPLING METHODS AND PROCEDURES	A-1
	Ontario Hydro Mercury Speciation Method (OH method)	A-1
	Continuous Mercury Monitors	A-4
	Atomic Fluorescence-Based Hg SCEMs	A-4
	Atomic Absorption-Based Hg SCEMs	A-4
	Flue Gas Pretreatment/Conversion	A-5
	Auxiliary Flue Gas Measurements	A-6
	O ₂ Determination	A-6
	CO ₂ Determination	A-6
	Chlorides, NH ₃ , and SO ₃	A-6

Reference	A-7
B MERCURY MEASUREMENTS	B-1
B.1 Mercury Measurements Made at Site S2	B-1
Complete OH Data Set	B-1
Coal Mercury and Chloride Analyses	B-2
B.2 Mercury Measurements Made at Site S4	B-3
Complete OH Data Set	B-3
B.3 Mercury Measurements Made at Site S5	B-5
Complete OH Data Set	B-5
B.4 Mercury Measurements Made at Site S6	B-8
Complete OH Data Set	B-8
C COMPLETE AUXILIARY FLUE GAS DATA FOR ALL SITES	C-1
D QUALITY ASSURANCE/QUALITY CONTROL	D-1
Ontario Hydro (OH) Method	D-1
Instrument Setup and Calibration.....	D-1
Presampling Preparation	D-2
Glassware and Plasticware Cleaning and Storage	D-2
Analytical Reagents.....	D-2
Blanks and Spikes	D-2
QA/QC Checks for Data Reduction and Validation.....	D-9
Data Reduction.....	D-9
Data Validation	D-9
Sample Identification and Chain of Custody	D-9
Personnel Responsibilities and Test Schedule	D-9
Test Site Organization	D-9
Test Preparations.....	D-10
Construction of Special Sampling Equipment and Modifications to the Facility	D-10
General Services Provided by the Facility.....	D-10
Access to Sampling Sites	D-10
Sample Recovery Areas	D-10
Test Personnel Responsibilities and Detailed Schedule	D-10
E SAMPLE CALCULATIONS	E-1

Volume of Gas Sample	E-1
Volume of Water Vapor	E-1
Water Vapor in the Gas Stream.....	E-2
Dry Molecular Weight.....	E-2
Molecular Weight	E-2
Average Stack Gas Velocity	E-2
Isokinetic Sampling Rate.....	E-3
Volume of Gas Sample Corrected to 3% O ₂	E-4
Mercury	E-4
F _d	E-4

LIST OF FIGURES

Figure 2-1 Schematic of Site S2 Showing Sample Locations from Horizontal and Vertical Perspectives	2-2
Figure 2-2 Plant Operation Data for Site S2	2-5
Figure 2-3 Comparison of Mercury Speciation Results 2001 and 2002 for Site S2	2-8
Figure 2-4 Hg SCEM Results for Site S2	2-10
Figure 2-5 Average Hg ²⁺ as Measured by Hg SCEMs (total Hg – Hg ⁰) for Site S2	2-11
Figure 3-1 Schematic of Site S4 Showing Sample Locations from a Vertical and Horizontal Perspective	3-2
Figure 3-2 Plant Operation Data for Site S4	3-4
Figure 3-3 Comparison of Mercury Speciation Results with the SCR in Service and with the SCR Bypassed	3-6
Figure 3-4 Comparison of Mercury Speciation Results 2001 and 2002 for Site S4	3-7
Figure 3-5 Hg SCEM Results for Site S4	3-8
Figure 3-6 Average Hg ²⁺ as Measured by Hg SCEMs (Total Hg–Hg ⁰) for Site S4	3-9
Figure 4-1 Schematic of Site S5 Showing Sample Locations for the Unit with the SCR from a Vertical and Horizontal Perspective	4-2
Figure 4-2 Schematic of Site S5 Showing Sample Locations for the Unit with No SCR from a Vertical and Horizontal Perspective	4-3
Figure 4-3 Plant Operation Data for Site S5 for the Unit with the SCR	4-5
Figure 4-4 Plant Operation Data for Site S5 for the Unit with No SCR	4-7
Figure 4-5 Comparison of Mercury Speciation Results with the SCR and Without an SCR at Site S5	4-11
Figure 4-6 Hg SCEM Results for Site S5 for the Unit with an SCR	4-12
Figure 4-7 Hg SCEM Results for Site S5 for the Unit with No SCR	4-13
Figure 5-1 Schematic of Site S6 Showing Sample Locations for Unit 1 with the SCR in Service from a Vertical and Horizontal Perspective	5-2
Figure 5-2 Schematic of Site S6 Showing Sample Locations for Unit 2 with the SCR Bypassed from a Vertical and Horizontal Perspective	5-3
Figure 5-3 Schematic of Site S6 Showing Sample Locations for Unit 4 with No SCR from a Vertical and Horizontal Perspective	5-4
Figure 5-4 Plant Operation Data for Site S6 for Unit 1 with the SCR in Service	5-7
Figure 5-5 Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed	5-9
Figure 5-6 Plant Operation Data for Site S5 for Unit 4 with No SCR	5-11
Figure 5-7 Comparison of Mercury Speciation Results for the Three Test Units	5-13

Figure 5-8 Hg SCEM Results for Site S6 for Unit 1 with the SCR in Service	5-15
Figure 5-9 Hg SCEM Results for Site S6 for Unit 2 with the SCR Bypassed	5-16
Figure 5-10 Hg SCEM Results for Site S6 for Unit 4 with No SCR	5-17
Figure 5-11 Average Hg ²⁺ as Measured by Hg SCEMs (total Hg - Hg ⁰) for Site S6 Unit 1 (SCR on-line)	5-18
Figure 5-12 Average Hg ²⁺ as Measured by Hg SCEMs (total Hg - Hg ⁰) for Site S6 Unit 2 (SCR bypassed)	5-19
Figure 5-13 Hg SCEM Results for Site S6 for Unit 2 with SCR Bypassed	5-19
Figure 6-1 Percent of Oxidized Hg ²⁺ at the Inlet of the SCR System as a Function of Chloride Content of the Coal	6-4
Figure 6-2 Mercury Speciation Results Comparing All the Sites Tested Firing Eastern Bituminous Coal	6-5
Figure 6-3 Comparison of Mercury Speciation Results from 2001 and 2002 at Site S2	6-7
Figure 6-4 Comparison of Mercury Speciation Results from 2001 and 2002 at Site S4	6-7
Figure A-1 Schematic of the OH Mercury Speciation Train	A-1
Figure A-2 Sample Recovery Scheme for the OH Mercury Speciation Train	A-3
Figure A-3 Schematic of the EERC Pretreatment/Conversion System for Use with Hg SCEMs	A-5

LIST OF TABLES

Table 1-1 Summary of Plant Configuration from 2001 Test Program	1-4
Table 2-1 Sampling Test Matrix for Site S2.....	2-3
Table 2-2 Average Auxiliary Flue Gas Data for Site S2.....	2-7
Table 2-3 OH Average and Percentage of Total Mercury Results for S2.....	2-7
Table 2-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S2	2-11
Table 2-5 Coal Analysis for Site S2.....	2-12
Table 2-6 Analysis of ESP Hopper Ash and FGD Material for Site S2.....	2-13
Table 2-7 NH ₃ Slip and SO ₃ Results at Site S2	2-13
Table 3-1 Sampling Test Matrix for Site S4.....	3-3
Table 3-2 Average Auxiliary Flue Gas Data for Site S4.....	3-5
Table 3-3 Average OH Mercury and Results for Site S4	3-6
Table 3-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S4	3-9
Table 3-5 Coal Analysis for Site S4.....	3-10
Table 3-6 Partitioning of Mercury in Material Collected from Venturi Scrubber.....	3-11
Table 3-7 S4 Flue Gas, NH ₃ Slip, and SO ₃ Results for Site S4	3-11
Table 3-8 Average Mercury Emission Factors for Site S4	3-12
Table 4-1 Sampling Test Matrix for Site S5.....	4-4
Table 4-2 Auxiliary Flue Gas Data for Site S5.....	4-9
Table 4-3 Average and Percentage of Total OH Mercury Results for S5.....	4-10
Table 4-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S5	4-14
Table 4-5 Coal Analysis for Site S5.....	4-15
Table 4-6 Analysis of ESP Hopper Ash.....	4-16
Table 4-7 Flue Gas SO ₃ and NH ₃ Results for Site S5	4-16
Table 4-8 Average Mercury Emission Factors for Site S5	4-17
Table 5-1 Specifications of Site S6 Units	5-1
Table 5-2 Sampling Test Matrix for Site S6.....	5-5
Table 5-3 Auxiliary Flue Gas Data for Site S6.....	5-12
Table 5-4 Average and Percentage of Total OH Mercury Results for S6.....	5-13
Table 5-5 Statistical Variation of the Mercury Results Based on the Hg SCEM Data for Site S6	5-18

Table 5-6 Coal Analysis for Site S6.....	5-20
Table 5-7 Analysis of ESP Hopper Ash.....	5-21
Table 5-8 Flue Gas SO ₃ and NH ₃ Results for Site S6	5-22
Table 5-9 Average Mercury Emission Factors for Site S6	5-22
Table 6-1 Summary of SCR Program Plant Configuration.....	6-2
Table 6-2 Average Analysis of Coals Fired During 2001 and 2002 Field Tests	6-3
Table 6-3 Change in Mercury Oxidation Across the SCR Catalyst	6-4
Table 6-4 Net Change in Hg ²⁺ as Measured at the Inlet to the Particulate Control Device.....	6-6
Table 6-5 Effect of the SCR on Hg ⁰ Concentration Across the Wet FGDs.....	6-8
Table 8-1 Elements of the QA/QC Plan.....	8-4
Table A-1 Sample Train Components for the OH Method	A-2
Table B-1 OH Mercury Data for Site S2 with the SCR in Service	B-1
Table B-2 Coal Analysis Completed at Site S2	B-2
Table B-3 OH Mercury Data for Site S4 with the SCR In Service	B-3
Table B-4 OH Mercury Data for Site S4 with the SCR Bypassed	B-4
Table B-5 OH Mercury Data for Site S5 for Unit with the SCR	B-5
Table B-6 OH Mercury Data for Site S5 for Unit Without an SCR.....	B-6
Table B-7 Coal Mercury and Chloride Analyses	B-7
Table B-8 OH Mercury Data for Site S6 for Unit 1 (SCR)	B-8
Table B-9 OH Mercury Data for Site S6 for Unit 2 (SCR bypassed)	B-9
Table B-10 OH Mercury Data for Site S6 for Unit 4 (no SCR)	B-10
Table B-11 Coal Mercury and Chloride Analyses for Site S6	B-10
Table C-1 Auxiliary Flue Gas Data for Site S2 with SCR in Service	C-1
Table C-2 Auxiliary Flue Gas Data for Site S4 with SCR in Service	C-2
Table C-3 Auxiliary Flue Gas Data for Site S4 with SCR Bypassed	C-3
Table C-4 Auxiliary Flue Gas Data for Site S5 for the Unit with an SCR.....	C-4
Table C-5 Auxiliary Flue Gas Data for Site S5 for the Unit Without an SCR.....	C-5
Table C-6 Auxiliary Flue Gas Data for Site S6 for Unit 1 (SCR)	C-6
Table C-7 Auxiliary Flue Gas Data for Site S6 for Unit 2 (SCR bypassed)	C-7
Table C-8 Auxiliary Flue Gas Data for Site S6 for Unit 4 (no SCR)	C-8
Table D-1 Results of Mercury Speciation Field Blanks at Site S2.....	D-3
Table D-2 Results of Mercury Speciation Field Spikes at Site S2.....	D-4
Table D-3 Results of Mercury Speciation Field Spikes at Site S4.....	D-5
Table D-4 Results of Mercury Speciation Field Blanks at Site S5.....	D-5
Table D-5 Results of Mercury Speciation Field Spikes at Site S5.....	D-6
Table D-6 Results of Mercury Speciation Field Blanks at Site S6.....	D-7
Table D-7 Results of Mercury Speciation Field Spikes at Site S6.....	D-8
Table D-8 Key Project Personnel	D-11

Table D-9 Test Personnel and Responsibilities..... D-12
Table D-10 Typical Test Schedule for a 4-Week Project..... D-13

1

INTRODUCTION

Coal combustion by electric utilities is a large source of anthropogenic mercury (Hg) emissions in the United States, according to the most recent data, accounting for 45 tons/yr of total point source Hg emissions [1]. In December 2000, the U.S. Environmental Protection Agency (EPA) issued an intent to regulate Hg from coal-fired utility boilers [2]. As a result, many utilities have become proactive in evaluating the effectiveness of current air pollution control technologies, as well as new technologies for Hg control [1,3–5].

Hg emissions from coal-fired boilers can be empirically classified, based on the capabilities of currently available analytical methods, into three main forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound Hg. Particulate-associated Hg (Hg_p) can be removed from flue gas by conventional air pollution control devices such as an electrostatic precipitator (ESP) or a baghouse. Hg^{2+} compounds are readily captured in flue gas desulfurization (FGD) units. Hg^0 is most likely to escape air pollution control devices and be emitted to the atmosphere. Total Hg concentrations in coal combustion flue gas typically range from 3 to 15 $\mu\text{g}/\text{Nm}^3$; however, Hg^0 , Hg^{2+} , and particulate-bound Hg concentrations are quite variable depending on coal composition and combustion conditions [6].

In addition to Hg, coal-burning power plants are a significant anthropogenic source of nitrogen oxide (NO_x) emissions to the atmosphere. NO_x emissions are an environmental concern primarily because they are associated with increased acidic precipitation, as well as fine-particle and ozone formation. Depending on the size and type of boiler, the 1990 Clean Air Act Amendments require specific reductions in NO_x emissions from coal-fired electric utilities. The most common NO_x reduction strategy is the installation of low- NO_x burners. These burners have the capability of reducing NO_x emissions by 40%–60%. However, with possible establishment of fine particulate ($\text{PM}_{2.5}$), regional haze, ozone regulations, and NO_x state implementation plans, there is increased incentive to reduce NO_x emissions to a level below what can be achieved using low- NO_x burners. Selective catalytic reduction (SCR) technology, which can reduce NO_x emissions by >90%, is, therefore, becoming more attractive, particularly because catalyst costs continue to decrease and the knowledge base for using SCR reactors is expanding. It is planned that approximately 100 gigawatts of coal-fired electrical capacity will have SCRs installed by 2005 [7].

1.1 Potential Impacts of SCR on Mercury Speciation

SCR units achieve lower NO_x emissions by catalytically reducing NO_x to N_2 and H_2O in the presence of ammonia (NH_3). The catalysts used in SCR units are generally metal oxides such as titanium dioxide (TiO_2)-supported vanadium oxide (V_2O_5). These units are generally operated at

about 650°–750°F (343°–399°C). Initial laboratory-scale testing indicated that metal oxides, including V₂O₅ and TiO₂, promoted the conversion of Hg⁰ to Hg²⁺ or particulate-bound Hg in relatively simple flue gas mixtures [8]. In addition, pilot- and full-scale Hg speciation measurements in European and U.S. coal-fired boilers equipped with SCR reactors have shown the potential to promote the formation of Hg²⁺ [9–11]. Therefore, it was hypothesized that the use of SCR may improve the Hg-control efficiency of existing air pollution control devices by promoting Hg²⁺ or particulate-bound Hg formation.

Possible mechanisms by which SCR operation could affect Hg speciation include:

- Catalytic oxidation of the Hg. Evidence indicates that vanadium-based catalysts can promote the formation of Hg²⁺ [9–12].
- Changing the flue gas chemistry. The significant reduction in flue gas NO_x and slight increase in NH₃ concentrations associated with SCR may affect Hg speciation. It is well known that NO_x, particularly NO₂, has a substantial effect on Hg speciation [13]. The gas-phase effects of NH₃ on Hg are unknown. SCR units also have the potential to catalyze the formation of sulfur trioxide (SO₃) and, potentially, chlorine (Cl₂), which may then react with Hg [14–18].
- The SCR unit provides additional residence time for the oxidation of Hg to take place.
- Changing the fly ash chemical composition. It is possible that SCR operation may change the surface chemistry of the fly ash particles such that their ability to adsorb or convert Hg species is altered.
- Increasing wall deposition. SCR systems may result in the deposition of ammonium bisulfate and ammonium sulfate in the air preheater and duct walls. It is unknown whether increased deposition could impact Hg emissions or speciation.

1.2 Pilot-Scale Screening Tests Conducted at the EERC

To investigate the effects of SCR on Hg speciation in a coal combustion system, EPRI, the U.S. Department of Energy (DOE), and EPA funded a pilot-scale project at the Energy & Environmental Research Center (EERC) [10]. The primary objective for the pilot-scale tests was to determine whether NH₃ injection or the catalyst in a representative SCR system promote the conversion of Hg⁰ to Hg²⁺ or particulate-bound Hg. Although this project was a screening evaluation and not a complete parametric study, it was designed to evaluate potential mechanisms for Hg conversion and the various coal parameters (like chemical composition) that may affect the degree of conversion.

Three bituminous coals and a Powder River Basin (PRB) subbituminous coal were burned in a pilot-scale combustion system equipped with an NH₃ injection system, SCR reactor, and ESP. The selection criteria for the four coals investigated were the significant differences in their sulfur and chloride contents.

The results from the tests indicated that NH₃ injection and, possibly, the SCR catalyst promote the conversion of Hg²⁺ to particulate-bound Hg in the coal combustion flue gases for two of the

bituminous coals, but this was not the case for the PRB coal. The results were inconclusive for the third bituminous coal. When the limited data are used in a linear regression analysis, it appears that the chloride, sulfur, and calcium contents of the coal correlate with Hg speciation across the SCR unit. Because of the inherent concerns related to small pilot-scale tests (surface area-to-volume ratios, different flue gas chemistries, and time and temperature profiles), it was decided that sampling at full-scale power plants was necessary. Therefore, beginning in 2001, EPRI, DOE, and EPA funded projects with the EERC and others to conduct Hg sampling at power plants with SCR technology.

1.3 2001 SCR Mercury Field-Sampling Project

The test program for 2001 was developed to address the limitations of pilot-scale testing by applying information obtained from previous work to several full-scale electric-generating facilities. A summary of plants and their configuration is provided in Table 1-1. The overall objective of 2001 testing was to evaluate the effects of SCR operation, selective noncatalytic reduction (SNCR), and flue gas conditioning on speciated Hg emissions at full-scale plants. More specifically, the objective was to evaluate Hg speciation across the unit as a result of these technologies. The results of testing conducted for the 2001 program are summarized below and can be found in “Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury” [11].

In general, data from 2001 testing indicated that SCR has the potential to increase Hg oxidation. However, significant differences in Hg speciation were observed between plants even with similar coal classifications. The possible reasons for these disparate differences likely include a combination of the following:

- Coal chloride concentration – The chloride level in the coal is the most straightforward approach to estimating Cl (HCl and Cl₂) in flue gas, although it is possible that alkalinity in the fly ash may tie up Cl and reduce its availability for some coals.
- Inlet percentage of Hg²⁺ – For plants with a high proportion of the inlet Hg already oxidized, the potential increase is much lower.
- Other flue gas constituents (e.g., alkalinity, SO₂, and SO₃).
- SCR system/catalyst properties – e.g., space velocity, area velocity, catalyst type, catalyst age, or number of catalyst layers.

It was thus theorized that the Hg speciation and associated oxidation of Hg across the SCR is highly dependent upon coal characteristics.

The primary conclusions from this effort were:

- At all four sites tested with SCR, an increase in Hg oxidation was observed across the SCR unit. It varied from 10% at Sites S1 and S3 to 71% at Site S4. SCR units can assist in converting Hg⁰ to Hg²⁺; however, the effect appears to be coal-specific and, possibly, catalyst-specific.

Table 1-1
Summary of Plant Configuration from 2001 Test Program

Site	Coal	Boiler Type	Boiler Size, MW	Low-NO _x Burners	Catalyst Vendor and Type	Catalyst Age	SCR Space Velocity, hr ⁻¹	Particulate Control	Sulfur Control
S1	PRB subbit.	Cyclone	650	No	Cormetech honeycomb	2 ozone seasons	1800	ESP	None
S2	OH bit.	Wall-fired	1300	Yes	Siemens/ Westinghouse plate	3 months	2125	ESP	Wet FGD ^a
S3	PA bit.	Tangential- fired	750	Yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	None
S4	KY bit.	Cyclone	650	No	Cormetech honeycomb	1 ozone season	2275	Venturi scrubber	Venturi scrubber

^a Flue gas desulfurization.

- For the two sites with SCR and wet FGD system (S2 and S4), a high percentage of the total Hg was removed, 89% and 90%, respectively. It should be noted that at Site S3 the percentage of Hg²⁺ at the outlet of ESP was 83%.
- Site S1 contained significant particulate-bound Hg, which was removed across the ESP, resulting in 85% total Hg removal. The high level of particulate-bound Hg may have been a result of the high carbon content of the ash (15% to 17%).
- Based on limited data (one site each), SNCR for NO_x control and NH₃ flue gas conditioning for improving ESP performance appeared to have a fairly small effect on Hg oxidation.

Upon review of 2001 test results, it was evident that additional data would be necessary to quantify the effect SCR operation had on Hg oxidation, including the following:

- Determine the effect of firing a PRB in a more typical configuration
- Determine the effect of firing a low-sulfur compliance coal
- Determine the effect of catalyst aging
- Determine the effect of catalyst type and space velocity

In order to address these issues, the program was expanded, and additional testing was conducted in 2002. It should be noted that the highest priority given was to test a plant with SCR and a pulverized coal (pc)-fired PRB coal. Unfortunately, no plant could be identified for testing in 2002 with this configuration. However, plans are being made to test two PRB plants with SCR units in 2003 and 2004.

1.4 Project Goals and Objectives

The project goal is to determine the impact of SCR operation on Hg speciation and on Hg emissions. The specific objectives of the 2002 testing were to:

- Determine the change in Hg speciation across the SCR catalyst as a function of catalyst aging (an additional ozone season). Two plants that had been tested in 2001 were retested in 2002.
- Determine the effect of firing a compliance (low-sulfur) coal on Hg speciation across the SCR catalyst.
- Determine what effects SCR has on subsequent Hg speciation and the overall Hg removal for the particulate control device and, if present, the wet FGD.

1.5 Sampling Approach

1.5.1 Mercury Sampling Using the Ontario Hydro Mercury Speciation Method

At each facility, the overall sampling approach consisted of measuring Hg across each pollution control device (SCR, ESP, and wet FGD). In this way, the effect of these devices on Hg could be determined. To determine the overall effect of SCR on Hg speciation and subsequent removal,

sampling was done at a unit with SCR followed by testing either at a similar unit without SCR or with SCR bypassed. For example, if a plant had an SCR unit, ESP and wet FGD unit samples were taken at five locations as follows:

- SCR inlet
- SCR outlet (prior to the air heater)
- ESP inlet (downstream of the air heater)
- ESP outlet
- Wet FGD outlet (generally the stack)

In general, samples were taken in pairs across each device (i.e., inlet and outlet of the SCR) and in duplicate or triplicate.

The Ontario Hydro (OH) sampling was done using EPA Method 17, ensuring that the filter was at the same temperature as the flue gas. At the SCR inlet and outlet condition, the OH sample filter averaged between 600° and 750°F (316° and 399°C). Following the air heater, the flue gas temperature was between 250° and 350°F (121° and 177°C). Sampling was done at a single point rather than traversing the flue gas duct. For wet stack locations where the flue gas temperature was below 250°F (121°C), an external heater (Method 5 configuration) was used to maintain the filter temperature above 250°F (121°C).

Based on the OH data, for each plant the following were calculated:

- The change in Hg oxidation across the SCR unit. This is defined as the difference in the percent Hg²⁺ in the flue gas between the outlet and inlet of the SCR unit.
- Overall effect of SCR on Hg oxidation. This is defined as the difference in the percentage of Hg²⁺ at the inlet to the particulate control device with and without SCR.
- Overall Hg removal. This is defined as percentage based on the difference in total Hg measured at the inlet to the particulate control device and the stack.

1.5.2 Mercury Sampling Using Hg SCEMs

Hg semicontinuous emission monitor (Hg SCCEM) testing was done using the PS Analytical (PSA) or Tekran system with a stannous chloride (wet-chemistry) conversion system. Attempts were made to operate the Hg SCEMs at inlet and outlet locations; however, it was extremely difficult to maintain Hg SCCEM operation on a continuous basis at locations upstream of particulate removal devices. Therefore, data from Hg SCEMs were collected primarily from ESP outlet or stack locations. Where applicable, OH data are compared to Hg SCCEM data; however, in general, OH results with appropriate quality control (QC) provide a more defensible EPA-approved method of quantifying Hg concentration and emissions. The benefit or advantage of Hg SCCEM operation is the real-time nature of the data. When operated continuously for several days, SCEMs provide valuable information on how Hg concentration and speciation changes with typical plant operation.