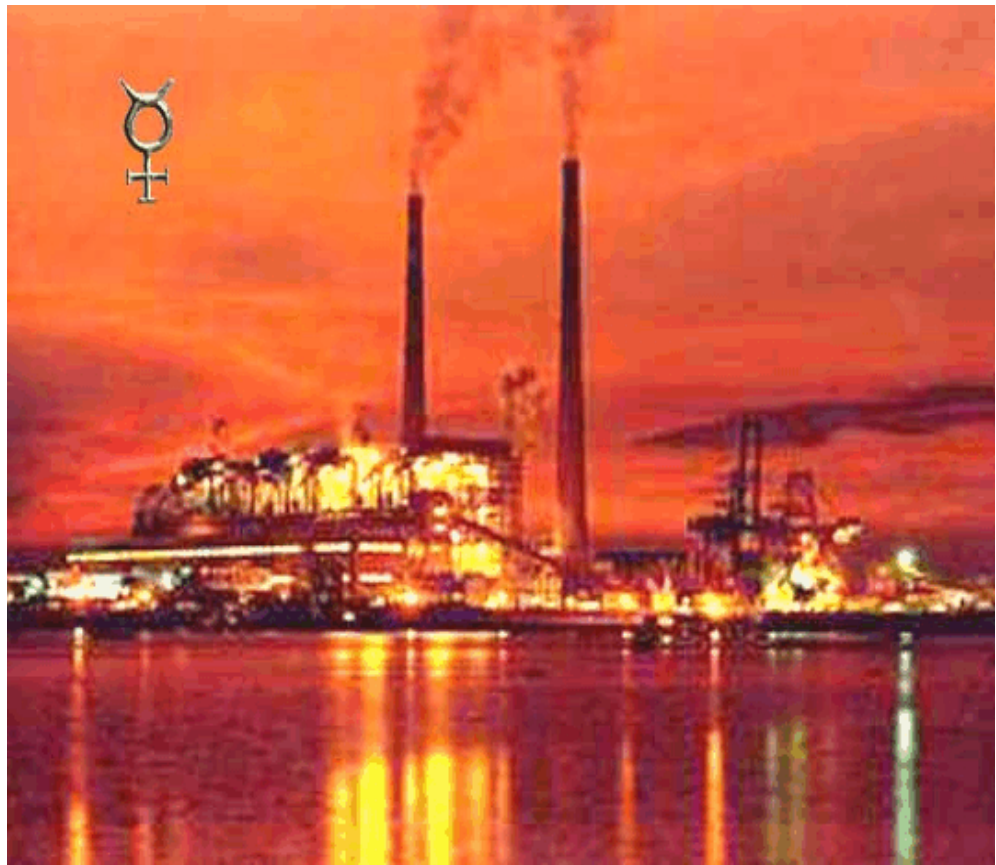




United States  
Environmental Protection  
Agency

EPA-600/R-04-147  
November 2004

# **EPRI Selective Catalytic Reduction Mercury Field Sampling Project**





# **Selective Catalytic Reduction Mercury Field Sampling Project**

by

Dennis L. Laudal, Jeffrey S. Thompson, Chad A. Wocken  
Energy & Environmental Research Center  
University of North Dakota  
PO Box 9018  
Grand Forks, ND 58202-9018

EPA Cooperative Agreement No. R 83060601

Project Officer: Chun Wai Lee  
U.S. Environmental Protection Agency  
Office of Research and Development  
National Risk Management Research Laboratory  
Air Pollution Prevention and Control Division  
Research Triangle Park, NC 27711

U.S. Environmental Protection Agency  
Washington DC 20460

## **Disclaimers**

This report was prepared as an account of work cosponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of DOE.

## **EERC DISCLAIMER**

LEGAL NOTICE: This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by EPA, EPRI, and DOE. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

# Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Acting Director  
National Risk Management Research  
Laboratory

## **EPA Review Notice**

This report has been peer and administratively reviewed by the U.S. Environmental Protection Agency and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

## Abstract

Many utilities are actively investigating methods to control and reduce mercury (Hg) emissions, particularly since EPA announced in 2000 its intent to regulate Hg emissions from coal-fired power plants. Even though this research has obtained some data, a lack of sound data still exists as to the effect of selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), and flue gas conditioning on the speciation and removal of Hg at power plants. Although both SCR and SNCR systems effectively reduce nitrogen oxide emissions, each system may impact Hg speciation differently. In addition, some utilities have utilized ammonia ( $\text{NH}_3$ ) or sulfur trioxide to improve electrostatic precipitator (ESP) performance, thereby changing the flue gas and ash chemistry.

This project investigates the impact that SCR, SNCR, and flue gas-conditioning systems have on total and speciated Hg emissions. If SCR or SNCR systems enhance Hg conversion/capture, then they could be thought of as multipollutant control technologies. Data from this project can be used for environmental planning purposes as well as to provide information for regulatory decisions. Previous Energy & Environmental Research Center pilot-scale tests investigated the role that coal type plays in Hg speciation, both with and without SCR. The results indicated that SCR, and possibly  $\text{NH}_3$  injection for flue gas conditioning, may enhance Hg capture, although it appeared that the impact was highly coal-specific. However, there were significant concerns as to the applicability of the pilot-scale results to full-scale power plants. To validate and expand the pilot-scale results, sampling was conducted at the full-scale level.

Twelve power plants were chosen for full-scale sampling to investigate the role that SCR, SNCR, flue gas conditioning, and coal blending have on Hg speciation. For a 10–12-day period, sampling was conducted both prior to and after the SCR unit or ESP using both the wet-chemistry Ontario Hydro method and near-real-time continuous Hg monitors. Hg variability, speciation, and concentration were evaluated. Fly ash and coal samples were also collected to obtain the Hg balance across the control devices.

The results indicate that SCR can assist in converting elemental Hg to oxidized Hg. However, the effect appears to be coal-specific and, possibly, catalyst-specific. Ammonia, whether injected directly as a gas or indirectly as urea, did not appear to have a significant

effect on Hg speciation and removal.

This project was a joint effort of EPRI, the U.S. Department of Energy National Energy Technology Laboratory, the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory, and the utility industry.

The cover illustration incorporates the Alchemist's symbol for mercury as shown in *Medicinisch-Chymisch- und Alchemistisches Oraculum*, Ulm, 1755 and is a little different from other renditions such as the one used in the Oak Ridge National Laboratory Website.



# Table of Contents

<u>Section</u>	<u>Page</u>
Abstract .....	v
List of Figures .....	viii
List of Tables .....	x
Nomenclature .....	xi
 Executive Summary .....	 1
Introduction .....	11
Potential Impacts of SCR on Hg Speciation .....	12
Pilot-Scale Screening Tests Conducted at the EERC .....	13
Experimental Approach .....	15
Results and Discussion .....	27
Effect of Flue Gas Conditioning and Coal Blending on Hg Speciation .....	27
Effect of an SCR on Hg Speciation .....	28
Effect of SCR Catalyst Age on Hg Speciation .....	32
SCR/Wet FGD Combination for Hg Control .....	34
Conclusions .....	37
References .....	39

## List of Figures

<u>Figure</u>	<u>Page</u>
ES-1 Non-elemental Hg concentrations at the inlet of the particulate control device with and without the SCR .....	6
ES-2 Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S2 .....	6
ES-3 Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S4 .....	7
1 Schematic of Site S1 showing sample locations from horizontal and vertical perspectives .....	19
2 Schematic of Site S2 showing sample locations from horizontal and vertical perspectives .....	19
3 Schematic of Site S3 showing sample locations from horizontal and vertical perspectives .....	20
4 Schematic of Site S4 showing sample locations from horizontal and vertical perspectives .....	20
5 Schematic of Site S5 for the unit with SCR showing sample locations from horizontal and vertical views .....	21
6 Schematic of Site S5 for the unit with no SCR showing sample locations from horizontal and vertical views .....	21
7 Schematic of Unit 1 at Site S6 with SCR in service showing sample locations from horizontal and vertical views .....	22
8 Schematic of Unit 2 at Site S6 with SCR bypassed showing sample locations from horizontal and vertical views .....	22
9 Side-view schematic of Site S8 Units 1 and 2 showing sampling locations .....	23
10 Schematic of Site S9 Units 1 and 2 showing sample locations from horizontal and vertical views .....	24
11 Schematic of Site A1 showing sample locations from horizontal and vertical views .....	25
12 Schematic of Site A2 showing sample locations from horizontal and vertical views .....	25
13 Schematic of Unit 2 at Site A3 showing sample locations from horizontal and vertical perspectives .....	26
14 Schematic of Site A4 showing sample locations from horizontal and vertical perspectives .....	26

## List of Figures (continued)

<u>Figure</u>	<u>Page</u>
15 Example of mercury variability at the stack from a site burning a high-sulfur eastern bituminous (Site S5) coal. . . . .	30
16 Percent of $\text{Hg}^{2+}$ at the inlet of the SCR system as a function of chloride content of the coal (note: data points without labels are results from plants without SCR units where Hg speciation was measured at the air heater inlet) . . . . .	30
17 Hg concentrations at the inlet of the particulate control device with and without the SCR . . . . .	31
18 CMM data showing the effect of bypassing the SCR reactor . . . . .	32
19 Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S2 . . . . .	33
20 Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S4 . . . . .	33

## List of Tables

<u>Table</u>	<u>Page</u>
ES-1 Configuration of Power Plants Tested .....	3
ES-2 Summary of Coal Analyses .....	4
ES-3 Change in Hg Oxidation Across the SCR Catalyst (95% confidence intervals) ..	5
ES-4 Effect of the SCR on Hg <sup>0</sup> Concentration Across the Wet FGDs (95% confidence intervals) .....	8
1. Configuration of Power Plants Tested .....	16
2. Summary of the Selection Criteria for Each Plant .....	17
3. Summary of Coal Analyses .....	18
4. Speciation Results at the ESP Inlet for Facilities With and Without Flue Gas Conditioning .....	28
5. Hg Speciation Results at the ESP Inlet When Blending PRB and Eastern Bituminous Coals .....	28
6. Change in Hg Oxidation Across the SCR Catalyst (95% confidence interval) .....	29
7. Effect of the SCR on Hg <sup>0</sup> Concentration Across the Wet FGDs .....	34

# Nomenclature

AH	air preheater
APCD	air pollution control device
Btu	British thermal units
CMM	continuous mercury monitor
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
FGD	flue gas desulfurization
Hg	mercury
Hg <sup>0</sup>	elemental mercury
Hg <sup>2+</sup>	oxidized mercury
Hg <sub>p</sub>	particulate-bound mercury
NH <sub>3</sub>	ammonia
NH <sub>4</sub> HSO <sub>4</sub>	ammonium bisulfate
NO <sub>x</sub>	nitrogen oxides
OH	Ontario Hydro mercury speciation method
PM <sub>2.5</sub>	particulate matter less than 2.5 μm
PRB	Powder River Basin
SCR	selective catalytic reduction of NO <sub>x</sub>
SNCR	selective noncatalytic reduction of NO <sub>x</sub>
SO <sub>3</sub>	sulfur trioxide
TiO <sub>2</sub>	titanium dioxide
V <sub>2</sub> O <sub>5</sub>	vanadium oxide

# Executive Summary

This report provides a summary of the results of the Selective Catalytic Reduction Mercury Field Sampling Project sponsored by EPRI, the U.S. Department of Energy (DOE) National Energy Technology Laboratory, the U.S. Environmental Protection Agency National Risk Management Research Laboratory, and the utility industry. This report outlines the field research conducted and the results.

## Introduction

During combustion, elemental mercury ( $\text{Hg}^0$ ) is liberated from coal. However, depending on the coal type, a significant fraction of the mercury (Hg) can be oxidized or can become associated with the fly ash particles in the post-combustion environment of a coal-fired boiler. Relative to  $\text{Hg}^0$ , oxidized Hg ( $\text{Hg}^{2+}$ ) and particulate-bound Hg ( $\text{Hg}_p$ ) are generally more effectively captured in conventional pollution control systems, such as flue gas desulfurization (FGD) systems, fabric filters, and electrostatic precipitators (ESPs) [1–4]. The identification of a process for converting  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and/or  $\text{Hg}_p$  forms could potentially improve the Hg removal efficiencies of existing pollution control systems.

## Potential Impacts of Selective Catalytic Reduction on Hg Speciation

Selective catalytic reduction (SCR) units achieve lower nitrogen oxide ( $\text{NO}_x$ ) emissions by using ammonia ( $\text{NH}_3$ ) to reduce  $\text{NO}_x$  to molecular nitrogen ( $\text{N}_2$ ) and  $\text{H}_2\text{O}$  over a catalyst. Laboratory, pilot-, and full-scale testing indicate that SCR catalysts promote the conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and/or  $\text{Hg}_p$  [5–7]. Possible mechanisms that could result in the SCR of  $\text{NO}_x$  impacting Hg speciation include:

- Catalytically oxidizing the Hg.
- Changing the flue gas chemistry.
- Providing additional residence time.
- Changing the fly ash chemical composition.

## Description of the Power Plants and Coal

For the purposes of this report, the plants using SCR (eight plants) are referred to as Sites S1 through S9. The two plants with flue gas conditioning are referred to as Sites A1 and A3; the plant using selective noncatalytic reduction (SNCR) (urea injection) is Site A2;

and the plant using different coal blends is Site A4. For consistency, the numbering system is the same that has been used for the annual reports. Site S7 is not included, as that site was not part of this project. Information about each of the plants and the coals fired at these plants is provided in Tables ES-1 and ES-2.

## **Effects of Flue Gas Conditioning and Fuel Blending on Hg Speciation**

At Site A1 Unit A, which fired a blend of 50% Powder River Basin (PRB) and 50% eastern bituminous, there was an increase in  $Hg_p$  with  $NH_3$  and sulfur trioxide ( $SO_3$ ) conditioning compared to  $SO_3$  conditioning alone. There was no difference at Unit B, where 100% PRB was fired.

At Site A2, urea was injected into the boiler producing  $NH_3$  gas (the SNCR process). Compared to the baseline case (no urea injection), the addition of urea had little if any effect on Hg speciation.

At Site A3 where ammonium bisulfate ( $NH_4HSO_4$ ) is added when firing 100% Texas lignite, the overall Hg removal (comparing the total Hg concentration at the ESP inlet and the stack) is about the same with and without  $NH_4HSO_4$ . However, without  $NH_4HSO_4$  injection, the removal is primarily by the wet FGD and with  $NH_4HSO_4$  injection, by the ESP. This is a result of an increase in  $Hg_p$  when  $NH_4HSO_4$  is added compared to the baseline case. When 20% PRB is added to the coal feed, there appears to be a decrease in the overall Hg removal (from less than 5% to around 50%).

At Site A4, tests were conducted at three different blend ratios of PRB and eastern bituminous coals with no flue gas-conditioning agents. Comparison of the results from each of the blends clearly shows an increase in  $Hg^0$  and decrease in  $Hg_p$  with an increase in the fraction of PRB in the blend.

## **Effect of SCR on Hg Speciation**

Table ES-3 presents results showing the impact of SCR operation on Hg oxidation. There is an increase in Hg oxidation across the SCR catalyst for those plants firing an eastern bituminous coal. The two plants that showed the lowest increase in oxidation across the SCR (S1 and S9) both fired 100% PRB coal. The amount of oxidation that occurs across the catalyst is highly variable. It appears to be affected by coal properties as well as catalyst design and, possibly, catalyst age.

Table ES-1. Configuration of Power Plants Tested

Plant <sup>a</sup>	NO <sub>x</sub> Control or Flue Gas Conditioning	Coal	Boiler Type	Boiler Size (MW)	Low-NO <sub>x</sub> Burners	Catalyst Vendor and Type	Catalyst Age <sup>b</sup>	SCR Space Velocity (hr <sup>-1</sup> )	Particulate Control	Sulfur Control
S1	SCR	PRB <sup>c</sup>	cyclone	650	no	Cormetech honeycomb	~8000 hr	1800	ESP	none
S2 <sup>d,e</sup>	SCR	OH bit. <sup>f</sup>	wall-fired	1300	yes	Siemens/ Westinghouse plate	1, 2, & 3 ozone seasons	2125	ESP	wet scrubber
S3	SCR	PA bit. <sup>g</sup>	tangentially fired	750	yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	none
S4 <sup>d,e</sup>	SCR	KY bit.	cyclone	650	no	Cormetech honeycomb	1, 2, & 3 ozone seasons	2275	Venturi scrubber	lime Venturi scrubber
S5	SCR	WV bit.	wall-fired	684	yes	Haldor Topsoe plate	3 months	3700	ESP	wet FGD
S6	SCR	low sulfur KY & WV bit.	concentrically fired	700	yes	Cormetech honeycomb	2 ozone seasons	3800	ESP	none
S8	SCR	PRB/bit. blend	wall-fired	820	yes	Cormetech honeycomb	2 months	3100	ESP	none
S9 <sup>d</sup>	SCR	PRB	opposed-fired	617	no	Cormetech honeycomb	3 months	2800	ESP	none
A1 Unit A	NH <sub>3</sub> /SO <sub>3</sub> <sup>h</sup> conditioning	PRB/bit. blend	opposed-fired	500	yes	NA <sup>i</sup>	NA	NA	ESP	none
A1 Unit B	NH <sub>3</sub> /SO <sub>3</sub> conditioning	PRB	opposed-fired	500	yes	NA	NA	NA	ESP	none
A2	SNCR	OH bit. <sup>g</sup>	tangentially fired	160	no	NA	NA	NA	ESP	none
A3	NH <sub>4</sub> HSO <sub>4</sub> <sup>j</sup> conditioning	TX lig. & TX lig./PRB blend	tangentially fired	793	no	NA	NA	NA	ESP	wet FGD
A4	none	3 PRB/bit. blends	wall-fired	156	no	NA	NA	NA	ESP	none

<sup>a</sup> Site S7 was not part of this project.<sup>b</sup> Approximate catalyst age at the time tested.<sup>c</sup> PRB = Powder River Basin<sup>d</sup> Two identical units sampled, one with and one without SCR.<sup>e</sup> Sampled three times, 1 year apart.<sup>f</sup> bit = bituminous.<sup>g</sup> Two different bituminous coals were used.<sup>h</sup> ammonia/sulfur trioxide.<sup>i</sup> NA = not applicable.<sup>j</sup> Ammonium bisulfate.<sup>k</sup> lig. = lignite



Table ES-2. Summary of Coal Analyses<sup>a</sup>

Constituent	S1 <sup>b</sup>	S2, Yr 1	S2, Yr 2	S2, Yr 3	S3	S4, Yr 1	S4, Yr 2	S4, Yr 3	S5	S6	S8 <sup>c</sup>	S9 <sup>b</sup>
Hg, µg/g dry	0.10	0.17	0.14	0.14	0.40	0.13	0.18	0.08	0.13	0.07	0.07	0.04
Chlorides, µg/g dry	<60	1333	523	411	1248	357	270	577	472	1020	1160	10
Moisture, %	27.5	7.6	6.1	10.3	7.0	10.5	8.3	7.0	4.6	6.1	19.3	30.3
Ash, %	3.7	11.7	9.4	8.7	14.0	9.1	9.1	9.1	12.1	11.6	6.6	5.4
Sulfur, %	0.19	3.9	3.9	2.8	1.7	2.9	3.0	3.3	3.6	1.0	1.4	0.40
Heating Value, Btu/lb	8960	11,092	12,097	11,803	11,421	11,341	12,077	12,260	12,120	12,019	12,721	8185

Constituent	A1 <sup>d</sup>	A1-B <sup>b</sup>	A2 <sup>e</sup>	A2 <sup>e</sup>	A3 <sup>f</sup>	A3 <sup>g</sup>	A4 <sup>b</sup>	A4 <sup>h</sup>	A4 <sup>i</sup>
Hg, µg/g dry	0.12	0.12	0.09	0.14	0.17	0.17	0.05	0.07	0.07
Chlorides, µg/g dry	806	153	1263	1087	133	18	18	210	241
Moisture, %	17.3	27.3	6.2	7.3	35.4	32.1	26	24	23.6
Ash, %	7.0	4.8	7.0	8.2	13	12.6	3.89	4.93	5.33
Sulfur, %	0.61	0.36	2.6	2.6	0.92	0.82	0.36	0.67	1.0
Heating Value, Btu/lb	10,377	9400	12,535	11,907	6147	7123	9078	9589	9744

<sup>a</sup> As-received unless otherwise noted.<sup>b</sup> 100% PRB coal.<sup>c</sup> Nominal 60% PRB and 40% eastern bituminous blend.<sup>d</sup> Nominal 50% PRB and 50% eastern bituminous blend.<sup>e</sup> Two different eastern bituminous coals.<sup>f</sup> 100% Texas lignite.<sup>g</sup> Nominal 80% Texas lignite and 20% PRB blend.<sup>h</sup> Nominal 85% PRB and 15% eastern bituminous blend.<sup>i</sup> Nominal 70% PRB and 30% eastern bituminous blend.

Table ES-3. Change in Hg Oxidation Across the SCR Catalyst (95% confidence intervals)

Site <sup>a</sup>	Year Sampled	SCR Inlet Hg <sup>2+</sup> , % of Total Hg	SCR Outlet Hg <sup>2+</sup> , % of Total Hg	Percentage Point Increase <sup>b</sup>
S1	2001	8	17	9
S2	2001	48±21	91±6	43
S2	2002	54±61	87±10	33
S2	2003	44±7	89±1	45
S3	2001	55±9	65±10	10
S4	2001	9±9	80±7	71
S4 <sup>c</sup>	2002	33±8	63±20	30
S4 <sup>c</sup>	2003	47±4	90±2	43
S5	2002	43±11	76±8	33
S6	2002	60±3	82±2	22
S8	2003	45±17	93±5	48
S9	2003	3±2	7±1	4

<sup>a</sup> Sites S1 and S9 fired a PRB coal; site S8 fired a blend of PRB and eastern bituminous coal; the others used only eastern bituminous coals; site S7 was not part of this project.

<sup>b</sup> Defined as (SCR outlet % - SCR inlet %) and based on the average value.

<sup>c</sup> Work was performed by Western Kentucky University.

Although there is strong evidence that an SCR catalyst does promote Hg oxidation, to determine the overall effect of SCR, it was useful to conduct tests both with and without SCR in service at each site. Figure ES-1 shows the comparison. For four of the six sites (S2 through S8) that fired eastern bituminous coal, there is a higher concentration of non-elemental Hg (Hg<sup>2+</sup> and Hg<sub>p</sub>) when an SCR unit was present, based on measurements made at the inlet to the particulate control device. For the other two sites, S3 and S6, non-elemental Hg was more than 90% of total Hg, both with and without an SCR unit in service. For the two sites that fired PRB coal (S1 and S9), there was very little increase in nonelemental Hg as a result of operating an SCR.

## Effect of SCR Catalyst Age on Hg 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 Hg oxidation potential of an SCR decrease with time?” Therefore, two of the facilities, S2 and S4, were tested over three years (both burned eastern bituminous coal). As Figures ES-2 and ES-3 show, there appears to be little, if any, aging effect over a 3-year period.

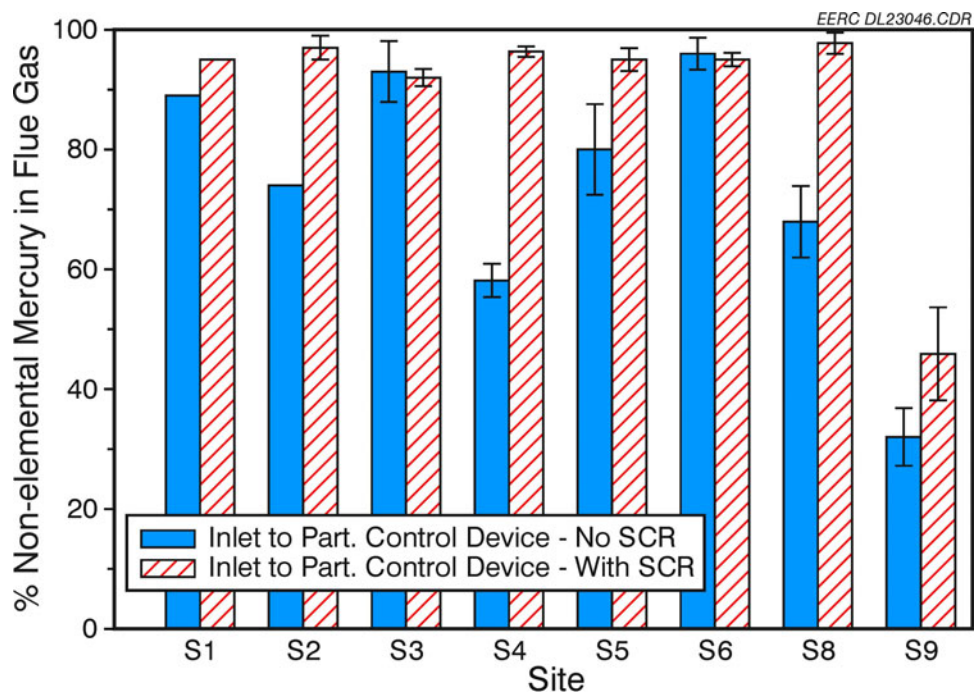


Figure ES-1. Non-elemental Hg concentrations at the inlet of the particulate control device with and without the SCR.

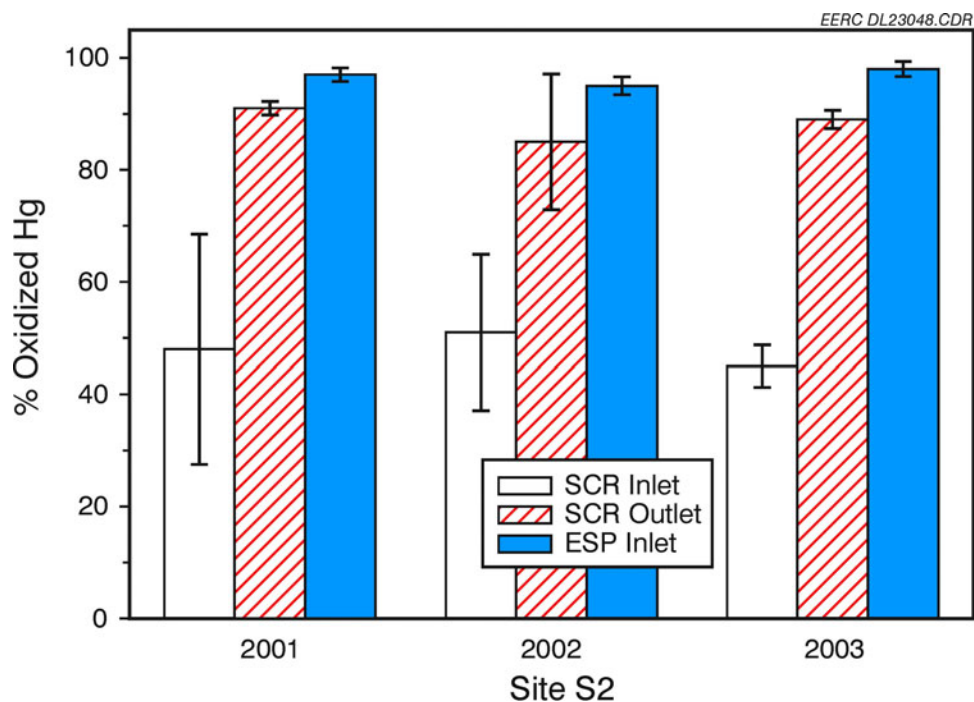


Figure ES-2. Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S2.

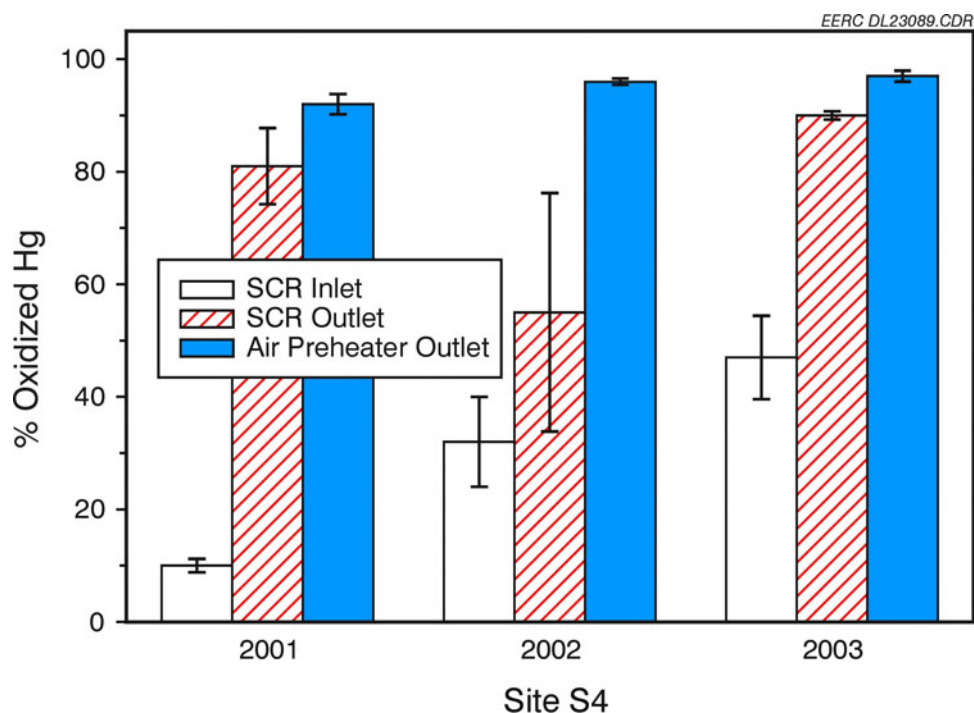


Figure ES-3 Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S4.

## Effect of the SCR on Wet FGD Performance for Hg Control

In general, wet FGDs remove more than 90% of  $\text{Hg}^{2+}$ . However, there is evidence that some of the captured  $\text{Hg}^{2+}$  can be reduced in the wet FGD to  $\text{Hg}^0$ . [6] 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 support this statement. As shown in Table ES-4, in all cases there is a percentage of  $\text{Hg}^{2+}$  that is chemically reduced to  $\text{Hg}^0$  in the wet FGD. This  $\text{Hg}^0$  is relatively insoluble and is, therefore, either reemitted or directly passes through the FGD, resulting in an increase of  $\text{Hg}^0$  across the FGD. Also, the data seem to indicate the operation of the SCR unit ameliorates this effect.

Table ES-4. Effect of the SCR on Hg<sup>0</sup> Concentration Across the Wet FGDs (95% confidence intervals)

Site	Year Sampled	FGD Inlet Hg <sup>0</sup> Conc., $\mu\text{g}/\text{Nm}^3$	FGD Outlet Hg <sup>0</sup> Conc., $\mu\text{g}/\text{Nm}^3$	Hg <sup>0</sup> Increase <sup>a</sup> , $\mu\text{g}/\text{Nm}^3$	Total Hg Removed, %
<i>With SCR</i>					
S2	2001	0.4±0.2 <sup>b</sup>	0.9±0.1	0.5	89
S2	2002	0.3±0.2	1.3±0.2	1.0	84
S2	2003	0.3±0.1	0.6±0.2	0.3	90
S4	2001	1.0±0.4	1.3±0.3	0.3	91
S4	2002	0.5±0.1	0.8±0.1	0.3	90
S4	2003	0.3±0.1	0.4±0.1	0.1	91
S5	2002	0.7±0.2	1.0±0.3	0.3	91
<i>Without SCR</i>					
S2	2001	3.4±0.1 <sup>b</sup>	5.0±1.0	1.6	51
S4	2001	5.6±1.0	7.1±0.2	1.5	46
S4	2002	5.7±0.6	8.0±1.3	2.3	44
S5	2002	4.7±1.0	6.1±0.6	1.4	51

<sup>a</sup> Defined as (FGD outlet Hg<sup>0</sup> conc. - FGD inlet Hg<sup>0</sup> conc.).

<sup>b</sup> The ESP inlet data were used for site S2 in 2001 because FGD inlet Hg concentration values are clear outliers.

## Conclusions

The primary conclusions based on the test results are:

- For plants firing eastern bituminous coals, Hg<sup>0</sup> can be oxidized across the SCR catalysts. The effect that SCR has on Hg speciation (i.e., extent of additional oxidation that occurs) depends on the coal characteristics and, possibly, catalyst properties. The increase of Hg<sup>2+</sup> at the SCR outlet ranged from 10% at Site S3 to 71% at Site S4.
- Over a 3-year period, catalyst age appears to have little effect on the oxidation potential of the SCR.
- Based on the limited data at three plants, SCR operation reduced the extent of Hg<sup>0</sup> reemission across a wet FGD.
- The effects of flue gas conditioning (including SNCR) on Hg speciation appears to be minimal. However, for the plant firing a Texas lignite, the addition of NH<sub>4</sub>HSO<sub>4</sub> did increase the percentage of Hg<sub>p</sub>.

## References

1. U.S. Environmental Protection Agency. *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Final Report to Congress*, EPA/453/R-98/004A [NTIS PB98-131774]; Office of Air Quality Planning and Standards and Office of Research and Development, Executive Summary, Feb 1998.
2. EPRI. *An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants*; EPRI Report No. 1000608; Oct 2000.
3. Hargrove, O.W. Jr.; Peterson, J.R.; Seeger, D.M.; Skarupa, R.C.; Moser, R.E. Update of EPRI Wet FGD Pilot-Scale Mercury Emissions Control Research. Presented at the EPRI–DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, ON, Canada, Aug 1995.
4. Holmes, M.J.; Redinger, K.E.; Evans, A.P.; Nolan, P.S. Control of Mercury in Conventional Flue Gas Emissions Control Systems. Presented at the Managing Hazardous Air Pollutants 4th International Conference, Washington, DC, Nov 12–14, 1997.
5. Gutberlet, H.; Schlüten, A.; Lienta, A. SCR Impacts on Mercury Emissions on Coal-Fired Boilers. Presented at the EPRI SCR Workshop, Memphis, TN, April 2000.
6. EPRI. *Pilot-Scale Screening Evaluation of the Impact of Selective Catalytic Reduction for NO<sub>x</sub> on Mercury Speciation*, EPRI Report No. 1000755, EPRI, Palo Alto, CA, 2000.
7. EPRI. *Power Plant Evaluation of the Effect of Selective Catalytic Reduction on Mercury*, EPRI Report No. 1005400, EPRI, Palo Alto, CA, 2002.



# Introduction

The objective of this report is to document the results and provide a summary of the tests associated with the “Selective Catalytic Reduction Mercury Field Sampling Project.” The testing was sponsored by EPRI, with additional funds provided by the utility industry, the U.S. Department of Energy (DOE) National Energy Technology Laboratory, and the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory. Over a 3-year period, mercury (Hg) measurements were completed at 12 power plants, 8 of which had selective catalytic reduction (SCR) for nitrogen oxides (NO<sub>x</sub>) reduction. Three of the plants injected ammonia (NH<sub>3</sub>) or NH<sub>3</sub> compounds either for conditioning electrostatic precipitators (ESPs) or for NO<sub>x</sub> reduction. The final plant was tested to help evaluate the effects on Hg speciation of blending Powder River Basin (PRB) subbituminous coal and eastern bituminous coals.

Coal combustion by electric utilities is a large source of anthropogenic 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, EPA issued an intent to regulate Hg from coal-fired utility boilers and, in 2004, issued a proposed rule for public comment. [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 Hg (Hg<sup>0</sup>), oxidized Hg (Hg<sup>2+</sup>), and particulate-bound Hg (Hg<sub>p</sub>). The Hg<sub>p</sub> can be removed from flue gas by conventional air pollution control devices (APCDs) such as an ESP or a baghouse. Hg<sup>2+</sup> compounds are readily captured in flue gas desulfurization (FGD) units. Hg<sup>0</sup> is most likely to escape APCDs and be emitted to the atmosphere. Total Hg concentrations in coal combustion flue gas typically range from 3 to 15 µg/Nm<sup>3</sup>; however, Hg<sup>0</sup>, Hg<sup>2+</sup>, and Hg<sub>p</sub> 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 NO<sub>x</sub> emissions to the atmosphere. These NO<sub>x</sub> 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  $\text{NO}_x$  emissions from coal-fired electric utilities. The most common  $\text{NO}_x$  reduction strategy is the installation of low- $\text{NO}_x$  burners. These burners have the capability of reducing  $\text{NO}_x$  emissions by 40%–60%. However, with possible establishment of fine particulate ( $\text{PM}_{2.5}$ ), regional haze, ozone regulations, and  $\text{NO}_x$  state implementation plans, there is increased incentive to reduce  $\text{NO}_x$  emissions to a level below what can be achieved using low- $\text{NO}_x$  burners. SCR technology, which can reduce  $\text{NO}_x$  emissions by more than 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]

## Potential Impacts of SCR on Hg Speciation

SCR units achieve lower  $\text{NO}_x$  emissions by catalytically reducing  $\text{NO}_x$  to molecular nitrogen ( $\text{N}_2$ ) and  $\text{H}_2\text{O}$  in the presence of  $\text{NH}_3$ . The catalysts used in SCR units are generally metal oxides such as titanium dioxide ( $\text{TiO}_2$ ) supported vanadium oxide ( $\text{V}_2\text{O}_5$ ). These units are generally operated at about 650–750 °F (343–399 °C). Initial laboratory-scale tests indicated that metal oxides, including  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$ , promoted the conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  or  $\text{Hg}_p$  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  $\text{Hg}^{2+}$ . [9–11] Therefore, it was hypothesized that the use of SCR may improve the Hg-control efficiency of existing APCDs by promoting  $\text{Hg}^{2+}$  or  $\text{Hg}_p$  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  $\text{Hg}^{2+}$ .
- Changing the flue gas chemistry. The significant reduction in flue gas  $\text{NO}_x$  and slight increase in  $\text{NH}_3$  concentrations associated with SCR may affect Hg speciation. It is well known that  $\text{NO}_x$ , particularly nitrogen dioxide ( $\text{NO}_2$ ), has a substantial effect on Hg speciation. [12] The gas-phase effects of  $\text{NH}_3$  on Hg are unknown. SCR units also have the potential to catalyze the formation of sulfur trioxide ( $\text{SO}_3$ ) and, potentially, alter the formation of chlorine, which may then react with Hg. [13–17]
- Providing 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.

## Pilot-Scale Screening Tests Conducted at the EERC

To investigate the effects of SCR on Hg speciation in a coal combustion system, EPRI, DOE, and EPA funded a pilot-scale project at the Energy & Environmental Research Center (EERC). [9] The primary objective for the pilot-scale tests was to determine whether  $\text{NH}_3$  injection or the catalyst in a representative SCR system promote the conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  or  $\text{Hg}_p$ . 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 PRB subbituminous coal were burned in a pilot-scale combustion system equipped with an  $\text{NH}_3$  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  $\text{NH}_3$  injection and, possibly, the SCR catalyst promote the conversion of  $\text{Hg}^{2+}$  to  $\text{Hg}_p$  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, EPA, and the utility industry funded projects with the EERC and others to conduct Hg sampling at power plants.



## Experimental Approach

The principal objective of the project was to determine the impact of SCR operation and flue gas conditioning on Hg speciation and, ultimately, on Hg emissions. To achieve this objective for each unit/coal, a sampling plan was developed for various operating conditions so that the effects of SCR or flue gas conditioning could be determined. At each site, tests were conducted (where feasible) under operating conditions with and without the SCR in operation or flue gas conditioning agents added. For the purposes of this report, the plants using SCR (eight plants) are referred to as Sites S1 through S9. The two plants with flue gas conditioning are referred to as Sites A1 and A3; the plant using selective noncatalytic reduction (SNCR) (urea injection) is Site A2; and the plant using different coal blends is Site A4. For consistency, the numbering system is the same that has been used for the annual reports. Site S7 is not included because that site was not part of this project. A summary of the configuration of each plant tested and the purpose for testing at that plant are provided in Tables 1 and 2, respectively.

During the first year of testing at the four sites with SCR (Sites S1, S2, S3, and S4), three conditions were evaluated. The first test condition was with the SCR unit on-line and fully operational. Specifically, the flue gas was passed through the SCR catalyst, and  $\text{NH}_3$  was added to reduce the  $\text{NO}_x$ . The second test condition was with the  $\text{NH}_3$  turned off. During this condition, the flue gas was flowing through the SCR, but no  $\text{NH}_3$  was added. The third was a baseline condition where SCR was either completely bypassed or a sister unit that did not have an SCR was tested. Based on the results of the first year of field work, it was decided that additional testing at plants with SCR would not include the  $\text{NH}_3$ -off test condition because it would not be expected that an SCR would be operated in this mode. Therefore, most of the subsequent work focused on the impact of SCRs on Hg speciation and emissions.

In addition to SCR, factors that were identified that could potentially contribute to Hg oxidation include coal type, specifically chlorine and sulfur content, and catalyst age. Therefore, at each plant, coal samples were taken and analyzed. A summary of coal data for each plant is provided in Table 3. Additionally, as shown in Table 2, two plants (Sites S2 and S4) were tested during each of 3 years to help determine the impact of catalyst age on

Table 1. Configuration of Power Plants Tested

Plant <sup>a</sup>	NO <sub>x</sub> Control or Flue Gas Conditioning	Coal	Boiler Type	Boiler Size (MW)	Low-NO <sub>x</sub> Burners	Catalyst Vendor and Type	Catalyst Age <sup>b</sup>	SCR Space Velocity (hr <sup>-1</sup> )	Particulate Control	Sulfur Control
S1	SCR	PRB <sup>c</sup>	cyclone	650	no	Cormetech honeycomb	~8000 hr	1800	ESP	none
S2 <sup>d,e</sup>	SCR	OH bit. <sup>f</sup>	wall-fired	1300	yes	Siemens/ Westinghouse plate	1, 2, & 3 ozone seasons	2125	ESP	wet scrubber
S3	SCR	PA bit. <sup>g</sup>	tangentially fired	750	yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	none
S4 <sup>d,e</sup>	SCR	KY bit.	cyclone	650	no	Cormetech honeycomb	1, 2, & 3 ozone seasons	2275	Venturi scrubber	lime Venturi scrubber
S5	SCR	WV bit.	wall-fired	684	yes	Haldor Topsoe plate	3 months	3700	ESP	wet FGD
S6	SCR	low sulfur KY & WV bit.	concentrically fired	700	yes	Cormetech honeycomb	2 ozone seasons	3800	ESP	none
S8	SCR	PRB/bit. blend	wall-fired	820	yes	Cormetech honeycomb	2 months	3100	ESP	none
91 S9 <sup>d</sup>	SCR	PRB	opposed-fired	617	no	Cormetech honeycomb	3 months	2800	ESP	none
A1 Unit A	NH <sub>3</sub> /SO <sub>3</sub> <sup>h</sup> conditioning	PRB/bit. blend	opposed-fired	500	yes	NA <sup>i</sup>	NA	NA	ESP	none
A1 Unit B	NH <sub>3</sub> /SO <sub>3</sub> conditioning	PRB	opposed-fired	500	yes	NA	NA	NA	ESP	none
A2	SNCR	OH bit. <sup>g</sup>	tangentially fired	160	no	NA	NA	NA	ESP	none
A3	NH <sub>4</sub> HSO <sub>4</sub> <sup>j</sup> conditioning	TX lig. & TX lig./PRB blend	tangentially fired	793	no	NA	NA	NA	ESP	wet FGD
A4	none	3 PRB/bit. blends	wall-fired	156	no	NA	NA	NA	ESP	none

<sup>a</sup> Site S7 was not part of this project.<sup>b</sup> Approximate catalyst age at the time tested.<sup>c</sup> PRB = Powder River Basin<sup>d</sup> Two identical units sampled, one with and one without SCR.<sup>e</sup> Sampled three times, 1 year apart.<sup>f</sup> bit = bituminous.<sup>g</sup> Two different bituminous coals were used.<sup>h</sup> ammonia/sulfur trioxide.<sup>i</sup> NA = not applicable.<sup>j</sup> Ammonium bisulfate.<sup>k</sup> lig. = lignite

Table 2. Summary of the Selection Criteria for Each Plant

Plant	Year Tested	Purpose of Test
S1	2001	PRB coal with SCR
S2	2001–2003	high-sulfur bituminous coal with SCR, a wet FGD system; catalyst aging effects
S3	2001	medium-sulfur bituminous coal with SCR
S4	2001–2003	high-sulfur bituminous coal with SCR, a wet FGD system; catalyst aging effects
S5	2002	high-sulfur bituminous coal with SCR, a wet FGD system
S6	2002	low-sulfur bituminous coal with SCR
S8	2003	PRB-bituminous coal blend with SCR
S9	2003	PRB coal with SCR
A1	2001	PRB and PRB-bituminous coal blends with $\text{NH}_3$ and $\text{SO}_3$ conditioning
A2	2001	medium-sulfur bituminous coal with SNCR
A3	2001	Texas lignate-PRB blends with $\text{NH}_4\text{HSO}_4$ conditioning
A4	2003	PRB-bituminous coal blends

Hg speciation and ultimately on Hg emissions. In addition to coal samples, in effort to complete a Hg balance at each plant, samples were collected from each of the APCDs. Schematics showing the sampling locations for each of the plants are shown in Figures 1–14. As can be seen in the figures, Ontario Hydro (OH) sampling was done at the inlet and outlet of each of the APCDs. In addition, continuous mercury monitors (CMMs) were located at all sampling locations after the particulate control device. Flue gas samples were also taken to measure the total particulate loading, chlorides,  $\text{SO}_3$  concentrations and, when the SCR was operating,  $\text{NH}_3$  slip, which is the amount of  $\text{NH}_3$  that passes unreacted through the SCR.

Table 3. Summary of Coal Analyses<sup>a</sup>

Constituent	S1 <sup>b</sup>	S2, Yr 1	S2, Yr 2	S2, Yr 3	S3	S4, Yr 1	S4, Yr 2	S4, Yr 3	S5	S6	S8 <sup>c</sup>	S9 <sup>b</sup>
Hg, µg/g dry	0.10	0.17	0.14	0.14	0.40	0.13	0.18	0.08	0.13	0.07	0.07	0.04
Chlorides, µg/g dry	<60	1333	523	411	1248	357	270	577	472	1020	1160	10
Moisture, %	27.5	7.6	6.1	10.3	7.0	10.5	8.3	7.0	4.6	6.1	19.3	30.3
Ash, %	3.7	11.7	9.4	8.7	14.0	9.1	9.1	9.1	12.1	11.6	6.6	5.4
Sulfur, %	0.19	3.9	3.9	2.8	1.7	2.9	3.0	3.3	3.6	1.0	1.4	0.40
Heating Value, Btu/lb	8960	11,092	12,097	11,803	11,421	11,341	12,077	12,260	12,120	12,019	12,721	8185

Constituent	A1 <sup>d</sup>	A1-B <sup>b</sup>	A2 <sup>e</sup>	A2 <sup>e</sup>	A3 <sup>f</sup>	A3 <sup>g</sup>	A4 <sup>b</sup>	A4 <sup>h</sup>	A4 <sup>i</sup>
Hg, µg/g dry	0.12	0.12	0.09	0.14	0.17	0.17	0.05	0.07	0.07
Chlorides, µg/g dry	806	153	1263	1087	133	18	18	210	241
Moisture, %	17.3	27.3	6.2	7.3	35.4	32.1	26	24	23.6
Ash, %	7.0	4.8	7.0	8.2	13	12.6	3.89	4.93	5.33
Sulfur, %	0.61	0.36	2.6	2.6	0.92	0.82	0.36	0.67	1.0
Heating Value, Btu/lb	10,377	9400	12,535	11,907	6147	7123	9078	9589	9744

<sup>a</sup> As-received unless otherwise noted.<sup>b</sup> 100% PRB coal.<sup>c</sup> Nominal 60% PRB and 40% eastern bituminous blend.<sup>d</sup> Nominal 50% PRB and 50% eastern bituminous blend.<sup>e</sup> Two different eastern bituminous coals.<sup>f</sup> 100% Texas lignite.<sup>g</sup> Nominal 80% Texas lignite and 20% PRB blend.<sup>h</sup> Nominal 85% PRB and 15% eastern bituminous blend.<sup>i</sup> Nominal 70% PRB and 30% eastern bituminous blend.

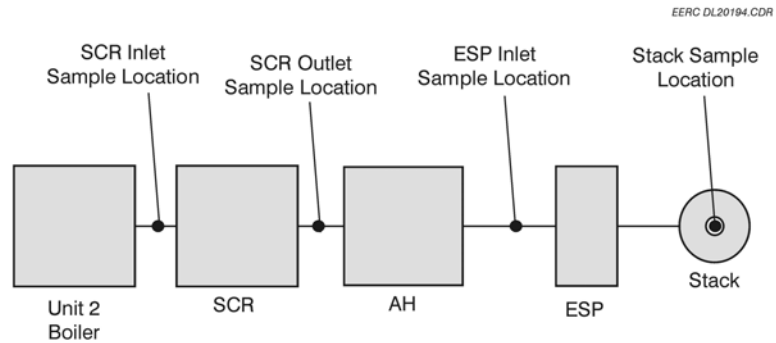
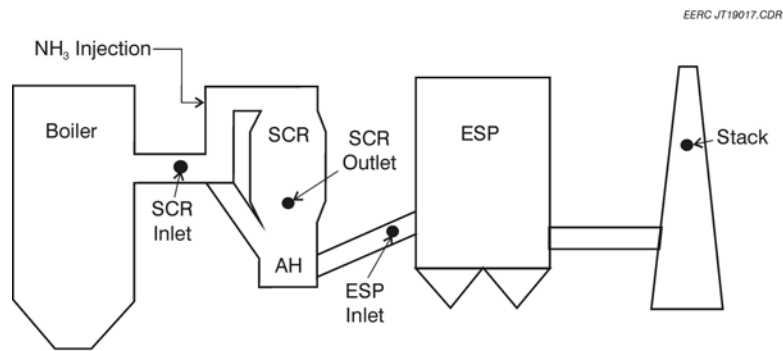


Figure 1. Schematic of Site S1 showing sample locations from horizontal and vertical perspectives (AH = air preheater).

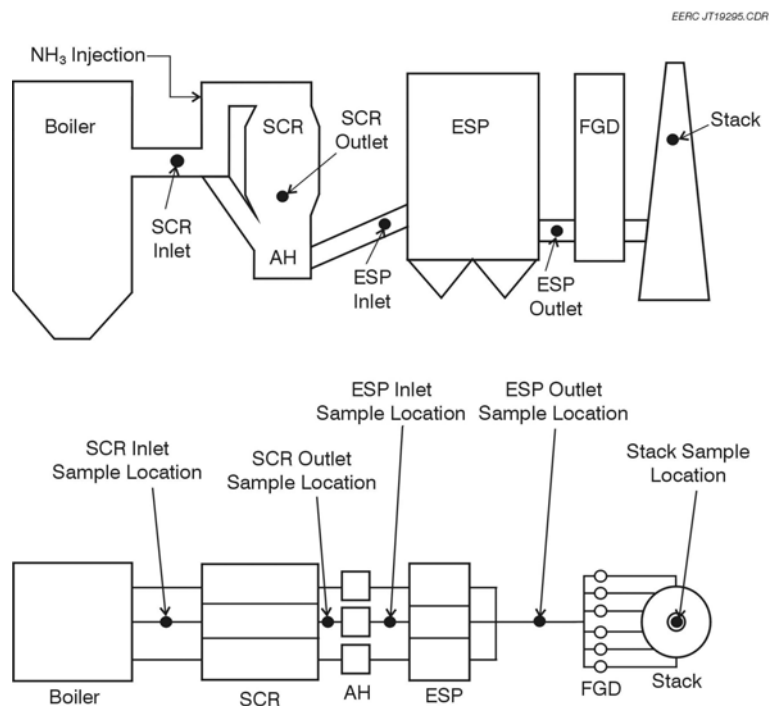


Figure 2. Schematic of Site S2 showing sample locations from horizontal and vertical perspectives (AH = air preheater).



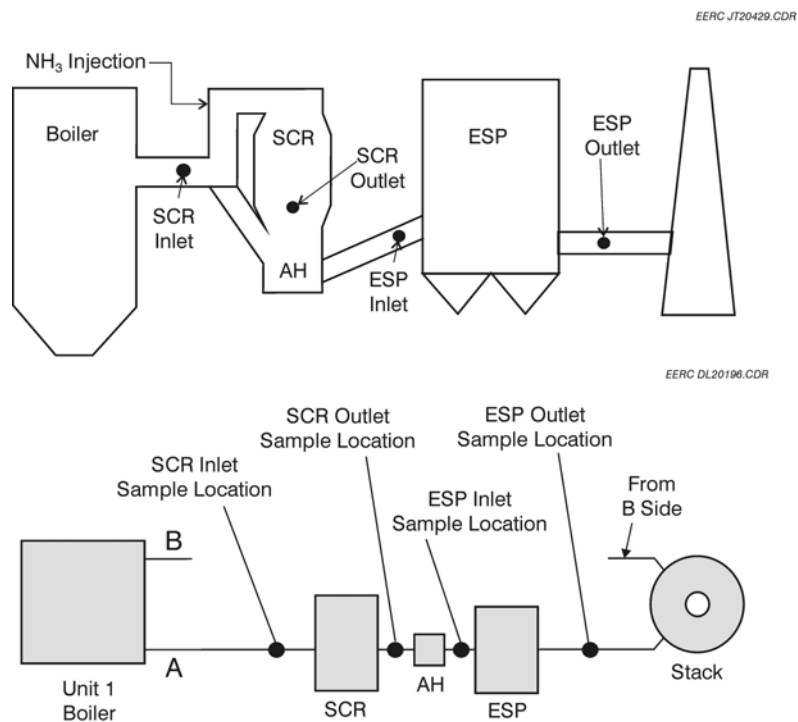


Figure 3. Schematic of Site S3 showing sample locations from horizontal and vertical perspectives (AH = air preheater).

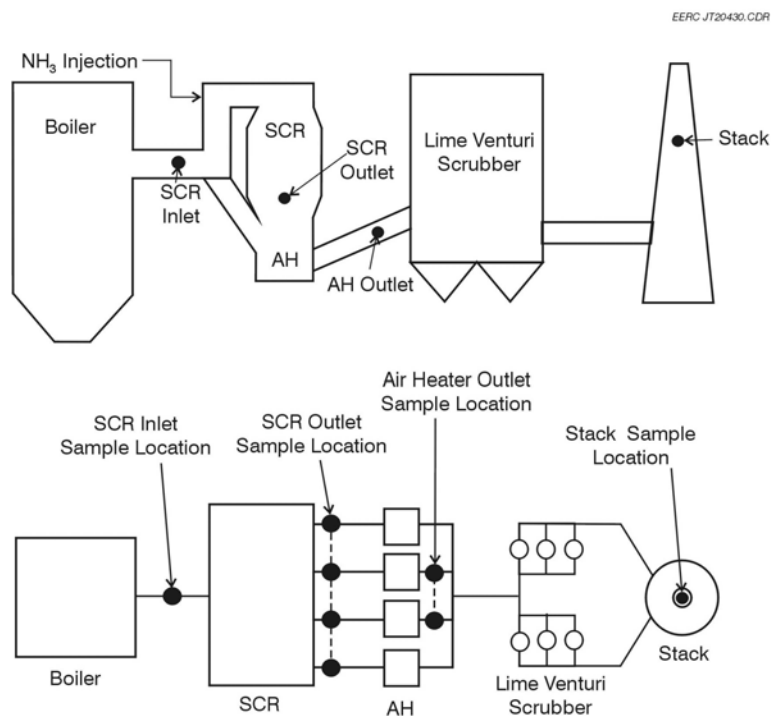


Figure 4. Schematic of Site S4 showing sample locations from horizontal and vertical perspectives (AH = air preheater).

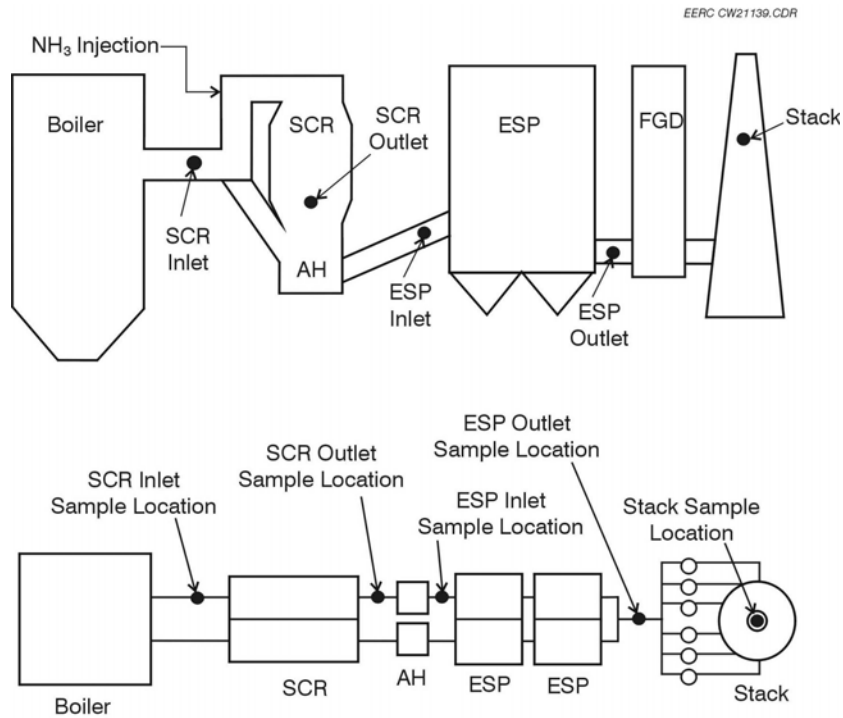


Figure 5. Schematic of Site S5 for the unit with SCR showing sample locations from horizontal and vertical views (AH = air preheater).

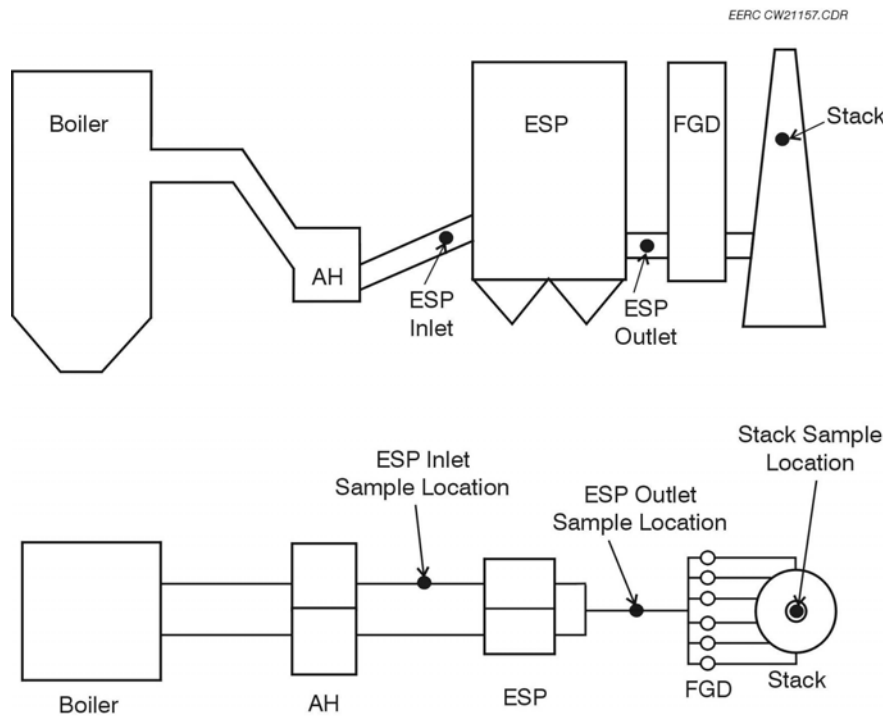


Figure 6. Schematic of Site S5 for the unit with no SCR showing sample locations from horizontal and vertical views (AH = air preheater).

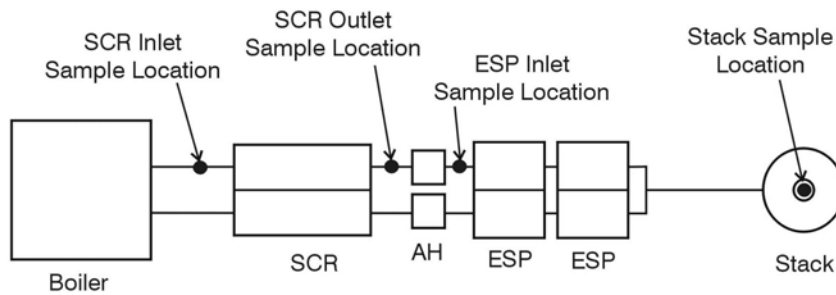
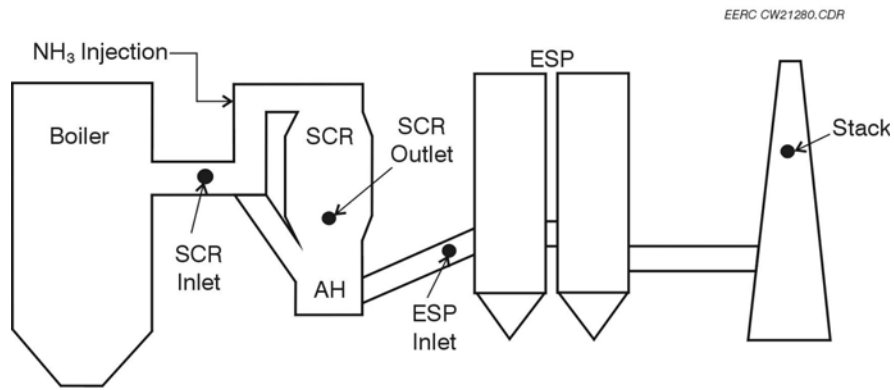


Figure 7. Schematic of Unit 1 at Site S6 with SCR in service showing sample locations from horizontal and vertical views (AH = air preheater).

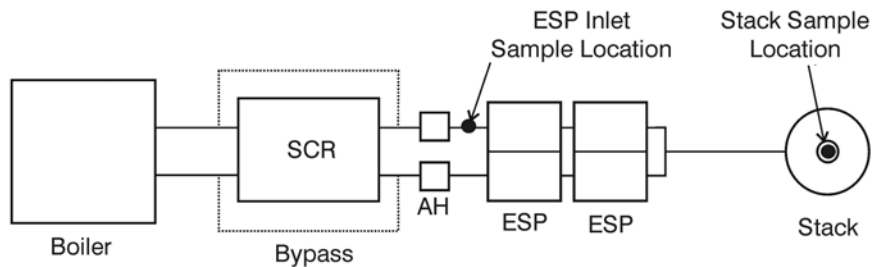
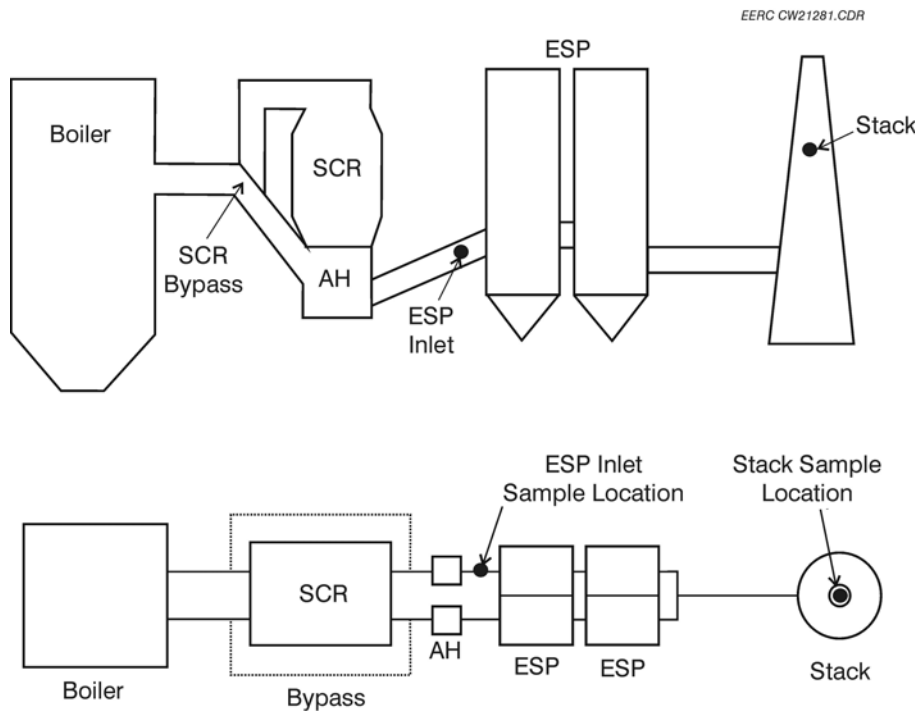


Figure 8. Schematic of Unit 2 at Site S6 with SCR bypassed showing sample locations from horizontal and vertical views (AH = air preheater).

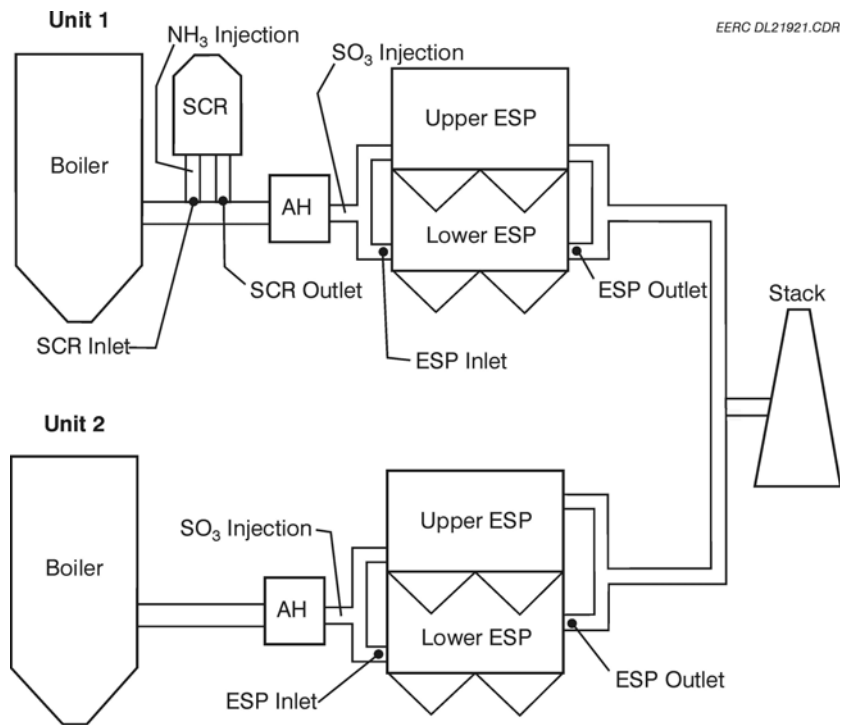


Figure 9. Side-view schematic of Site S8 Units 1 and 2 showing sampling locations (AH = air preheater).

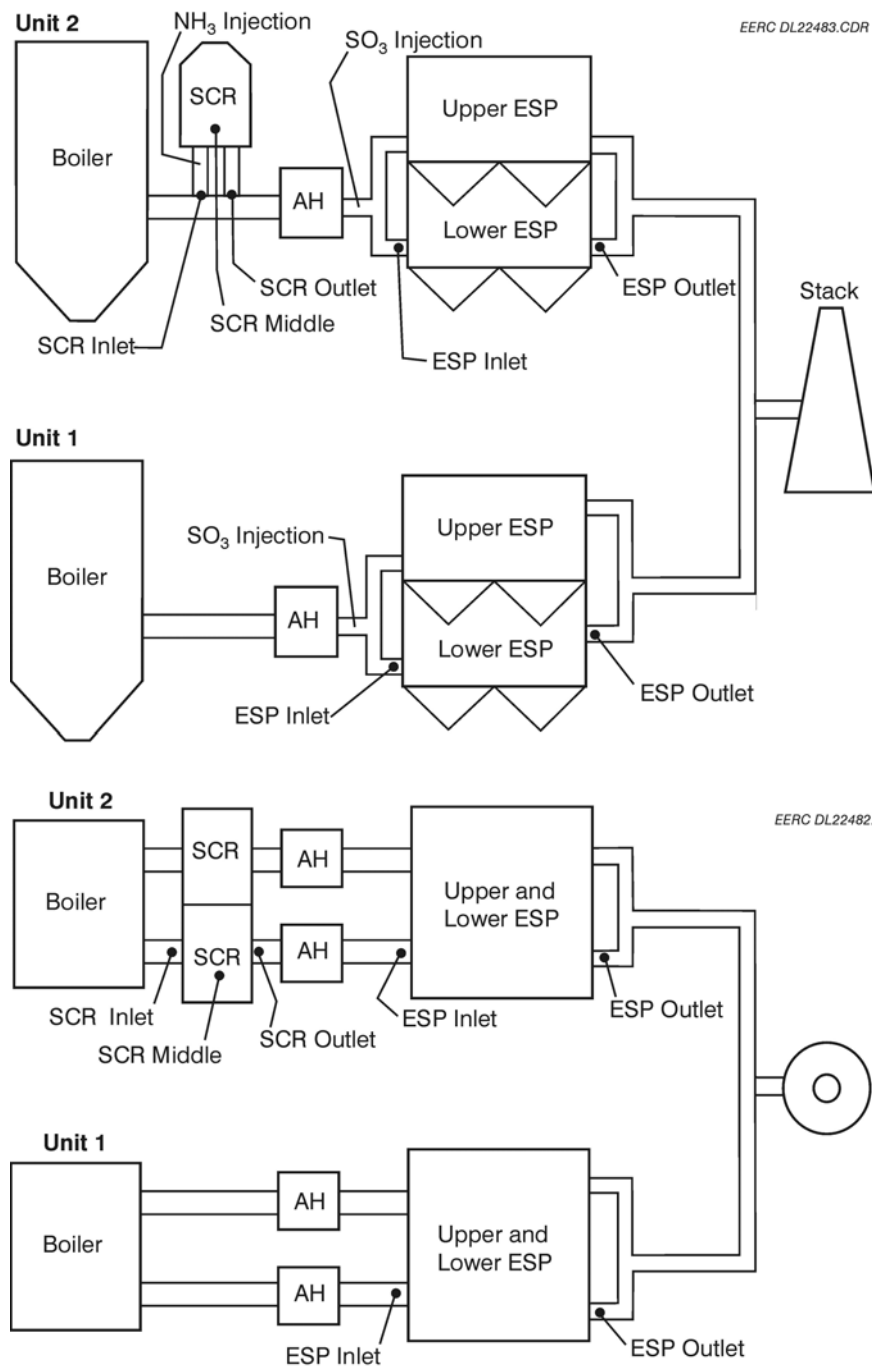


Figure 10. Schematic of Site S9 Units 1 and 2 showing sample locations from horizontal and vertical views (AH = air preheater).

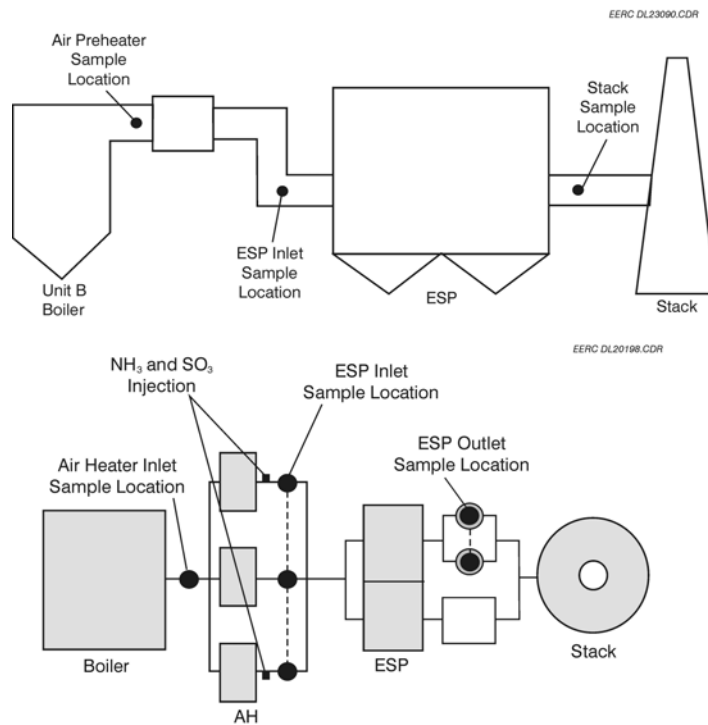


Figure 11. Schematic of Site A1 showing sample locations from horizontal and vertical views (AH = air preheater).

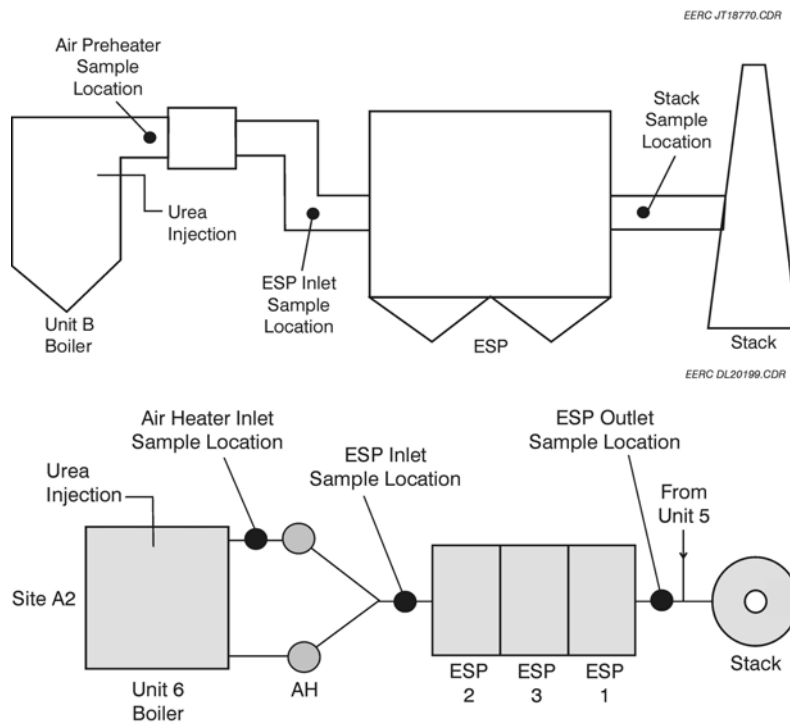


Figure 12. Schematic of Site A2 showing sample locations from horizontal and vertical views (AH = air preheater).

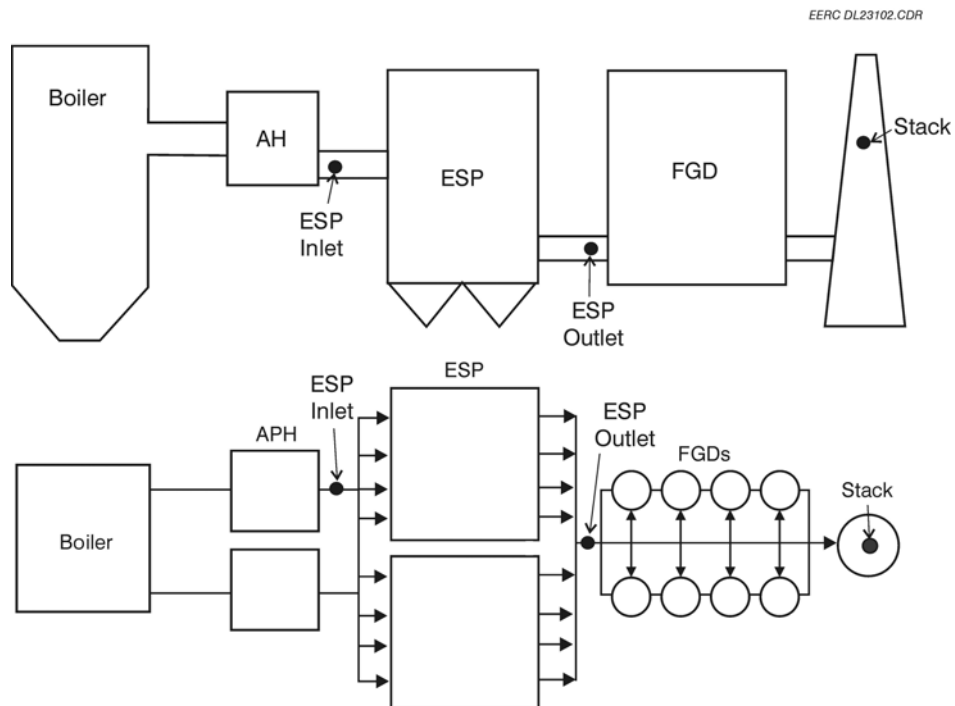


Figure 13. Schematic of Unit 2 at Site A3 showing sample locations from horizontal and vertical perspectives (AH = air preheater).

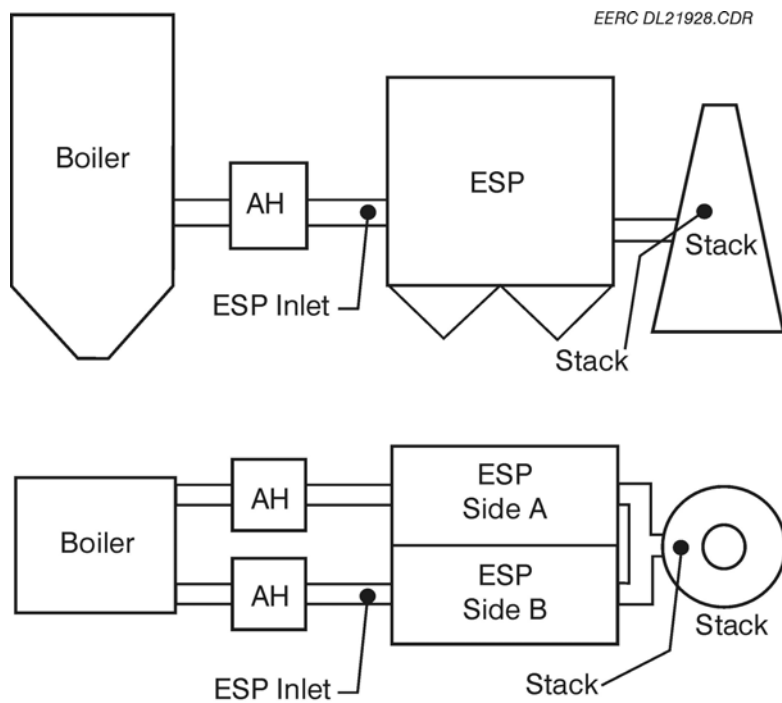


Figure 14. Schematic of Site A4 showing sample locations from horizontal and vertical perspectives (AH = air preheater).

## Results and Discussion

The primary focus of this project was to evaluate changes in flue gas chemistry and determine how this impacts Hg speciation. This was accomplished by testing at facilities that fired different coals and had different APCDs, as shown in Table 1. As stated previously, the use of SCR to reduce NO<sub>x</sub> emissions has the potential to improve the Hg control efficiency of existing particulate removal and FGD systems by promoting Hg<sup>2+</sup> or Hg<sub>p</sub> formation. As data were compiled at the various facilities, several factors were identified which may potentially impact the oxidation potential of SCR. Among these factors, coal type and catalyst type, structure, and age were specifically identified as factors that have the potential to influence Hg speciation.

To evaluate the effect of SCR on Hg speciation and, ultimately, on Hg emission at each plant, the following were determined:

- The change in Hg oxidation across the SCR unit.
- The effect of SCR on Hg oxidation at the particulate control device (obtained by comparing Hg speciation results with and without SCR in service).
- The overall Hg removal with and without SCR.

The following is a summary discussion of the results. Detailed results were presented in the annual reports submitted in 2001 and 2002 as well as individual reports of the plants sampled in 2003 (see bibliography of project reports).

### Effect of Flue Gas Conditioning and Coal Blending on Hg Speciation

The results of the tests at the three facilities where flue gas conditioning agents were used to enhance ESP performance are shown in Table 4. At Sites A1 and A3, it appeared that NH<sub>3</sub> injection tends to increase Hg<sub>p</sub> but inhibits Hg oxidation. It must be stressed that these are very limited tests, and the results are quite variable. In fact, at Site A2, where urea was injected into the boiler, the results are somewhat different. Here there was little effect on the Hg<sub>p</sub>, and the effect of urea injection on Hg oxidation appeared to give different results for the two coals tested. It is unknown if this was because NH<sub>3</sub> is injected at a much higher temperature compared to NH<sub>3</sub> injection to improve ESP performance or if the effect is simply coal dependent. In Table 5, the results are shown when different blends of a PRB and



an eastern bituminous coal are fired. The results are what would be expected; there is a decrease in  $Hg_p$  and an increase in  $Hg^0$  when increasing amounts of PRB are used in the blend.

Table 4. Hg Speciation Results at the ESP Inlet for Facilities With and Without Flue Gas Conditioning

Hg Species	A1-1 <sup>a</sup>		A1-2		A2-1 <sup>b</sup>		A2-2		A3-1 <sup>c</sup>		A3-1	
	50% PRB <sup>d</sup> & 50% Bit. <sup>e</sup>		100% PRB		100% Bit. Coal 1		100% Bit. Coal 2		100% TX Lig. <sup>f</sup>		80% TX Lig. & 20% PRB	
	with	without	with	without	with	without	with	without	with	without	with	without
$Hg_p$ , %	80	50	11	9	1	2	1	8	54	24	28	5
$Hg^0$ , %	2	7	67	72	37	17	12	13	10	10	35	17
$Hg^{2+}$ , %	18	43	22	19	62	81	87	79	36	66	37	78
Total Hg removed	65.3	45.8	21.1	9.8	19.2	-11.4	0.1	1.8	75.5	75.6	51.9	48.4

<sup>a</sup> A1 used both  $NH_3$  and  $SO_3$  injected just upstream of the ESPs. Only the  $NH_3$  was turned off for tests without conditioning.

<sup>b</sup> A2 was an SNCR unit, so urea was injected into the boiler.

<sup>c</sup> A3 injected  $NH_4HSO_4$  just upstream of the ESPs.

<sup>d</sup> PRB = Powder River Basin.

<sup>e</sup> Bit. = bituminous.

<sup>f</sup> Lig. = lignite.

Table 5. Hg Speciation Results at the ESP Inlet When Blending PRB and Eastern Bituminous Coals

Hg Species	A4-1	A4-2	A4-3
	70% PRB <sup>d</sup> & 30% Bit. <sup>e</sup>	85% PRB & 15% Bit.	100% PRB
$Hg_p$ , %	46	13	1
$Hg^0$ , %	20	53	95
$Hg^{2+}$ , %	35	34	4
Total Hg removed	47.3	23.7	6.3

<sup>a</sup> PRB = Powder River Basin.

<sup>b</sup> Bit. = bituminous.

## Effect of an SCR on Hg Speciation

The percentage of  $Hg^{2+}$  was measured at both the inlet and outlet of the SCR unit at each facility. It should be noted that all of the OH samples taken at these two locations were prior to the air preheater; therefore, the temperature ranged from 640 to 700 °F (338 to 371 °C).

Table 6 presents the results for all of the plants tested that had SCR. In all cases, there was

an increase in Hg oxidation across the SCR catalyst. However, the amount of oxidation that occurs across the catalyst is highly variable. Some factors that may have affected the level of oxidation are coal type and catalyst chemistry, structure, and age.

Table 6. Change in Hg Oxidation Across the SCR Catalyst (95% confidence interval)

Site <sup>a</sup>	Year Sampled	SCR Inlet Hg <sup>2+</sup> , % of Total Hg	SCR Outlet Hg <sup>2+</sup> , % of Total Hg	Percentage Point Increase <sup>b</sup>
S1	2001	8	17	9
S2	2001	48±21	91±6	43
S2	2002	54±61	87±10	33
S2	2003	44±7	89±1	45
S3	2001	55±9	65±10	10
S4	2001	9±9	80±7	71
S4 <sup>c</sup>	2002	33±8	63±20	30
S4 <sup>c</sup>	2003	47±4	90±2	43
S5	2002	43±11	76±8	33
S6	2002	60±3	82±2	22
S8	2003	45±17	93±5	48
S9	2003	3±2	7±1	4

<sup>a</sup> Sites S1 and S9 fired a PRB coal; site S8 fired a blend of PRB and eastern bituminous coal; the others used only eastern bituminous coals; site S7 was not part of this project.

<sup>b</sup> Defined as (SCR outlet % - SCR inlet %) and based on the average value.

<sup>c</sup> Work was performed by Western Kentucky University.

There was substantial variability in the percentage of Hg<sup>2+</sup> at both the SCR inlet and outlet locations. An example showing this variability is shown in Figure 15. However, there was also variability among the other sites firing eastern bituminous coal. For example, repeat testing conducted at Site S4 indicated a substantial increase in the percentage of Hg<sup>2+</sup> when the coal chloride concentration increased from 2001 to 2002 testing. As shown in Figure 16, one factor that appears to relate to the percentage of Hg<sup>2+</sup> at the inlet to SCR unit is the chloride concentration in the coal. It appears there is a threshold chloride concentration at about 300–500 ppm chloride above which 40%–60% Hg oxidation results at the SCR inlet. What effect this has on overall Hg oxidation is unclear.

Factors that may affect Hg oxidation are catalyst type and space velocity. Without substantially more data, it is very difficult to determine the effects of these parameters. For example, Sites S2 and S4 had space velocities less than 2300 hr<sup>-1</sup>; Sites S3, S5, and S6 had

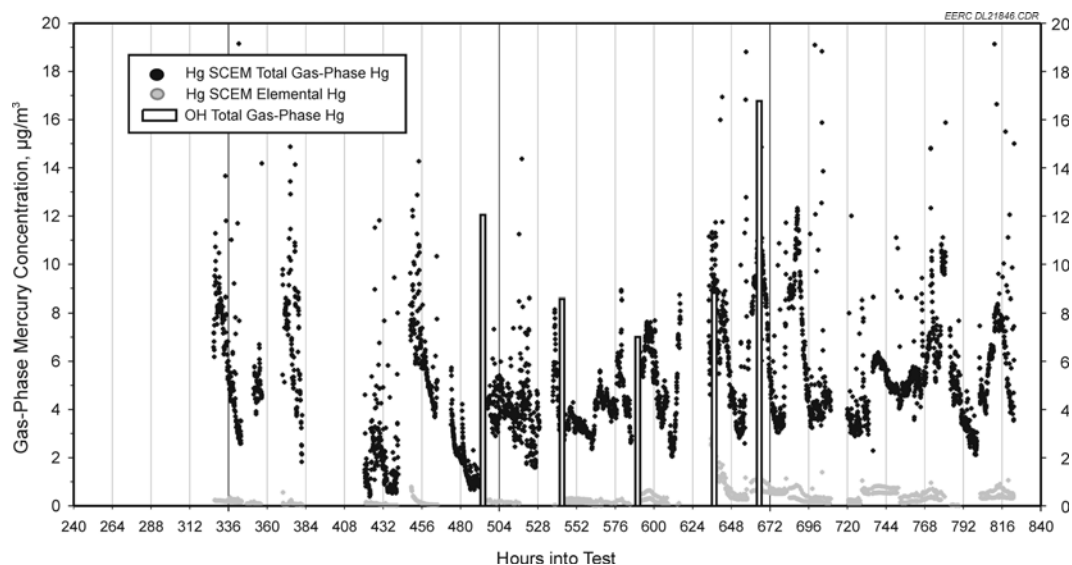


Figure 15. Example of mercury variability at the stack from a site burning a high-sulfur eastern bituminous (Site S5) coal.

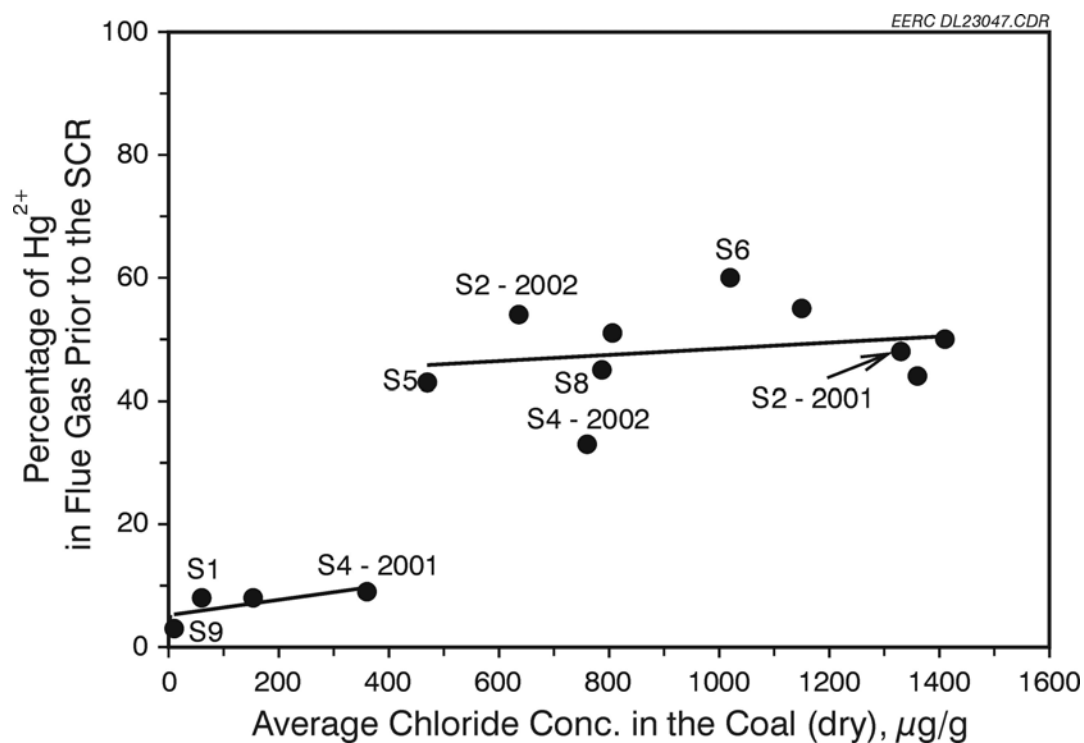


Figure 16. Percent of  $\text{Hg}^{2+}$  at the inlet of the SCR system as a function of chloride content of the coal (note: data points without labels are results from plants without SCR units where Hg speciation was measured at the air heater inlet).

space velocities greater than  $3700 \text{ hr}^{-1}$ ; but there does not appear to be a clear correlation. However, as shown in Table 1, the catalysts were also different. An attempt was made to evaluate catalyst aging effects by retesting two plants (Sites S2 and S4). The results are discussed in next section. EPRI is currently in the process of trying to develop models that would predict the effects of the SCR catalysts based on catalyst properties.

Although there is strong evidence that an SCR catalyst does promote Hg oxidation, to determine the overall effect of SCR, it was useful to conduct tests both with and without SCR in service at each site. Figure 17 shows the comparison. For three of the five sites, there is a higher concentration of non-elemental Hg ( $\text{Hg}^{2+}$  and  $\text{Hg}_p$ ) when an SCR unit was present based on measurements made at the inlet to the particulate control device. For the other two sites, S3 and S6, non-elemental Hg was greater than 90% of the total both with and without an SCR unit in service. Once the SCR unit is bypassed, the change in Hg oxidation occurs rapidly, as is shown by the CMM data presented in Figure 18.

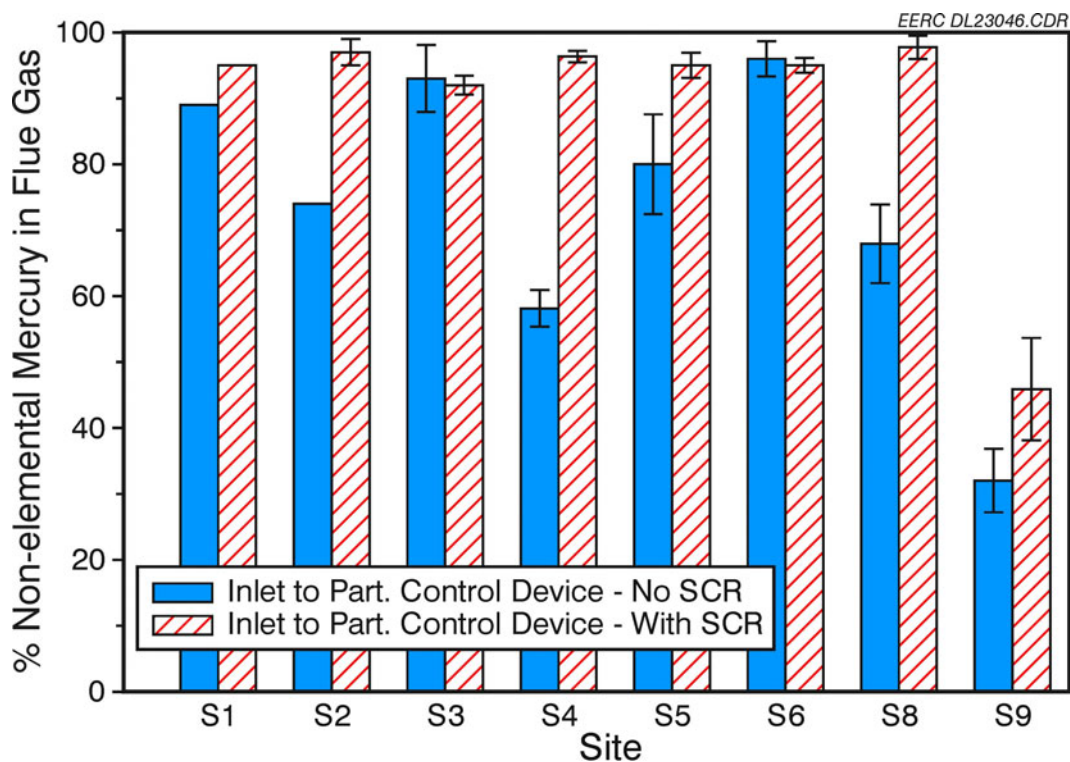


Figure 17. Hg concentrations at the inlet of the particulate control device with and without the SCR.

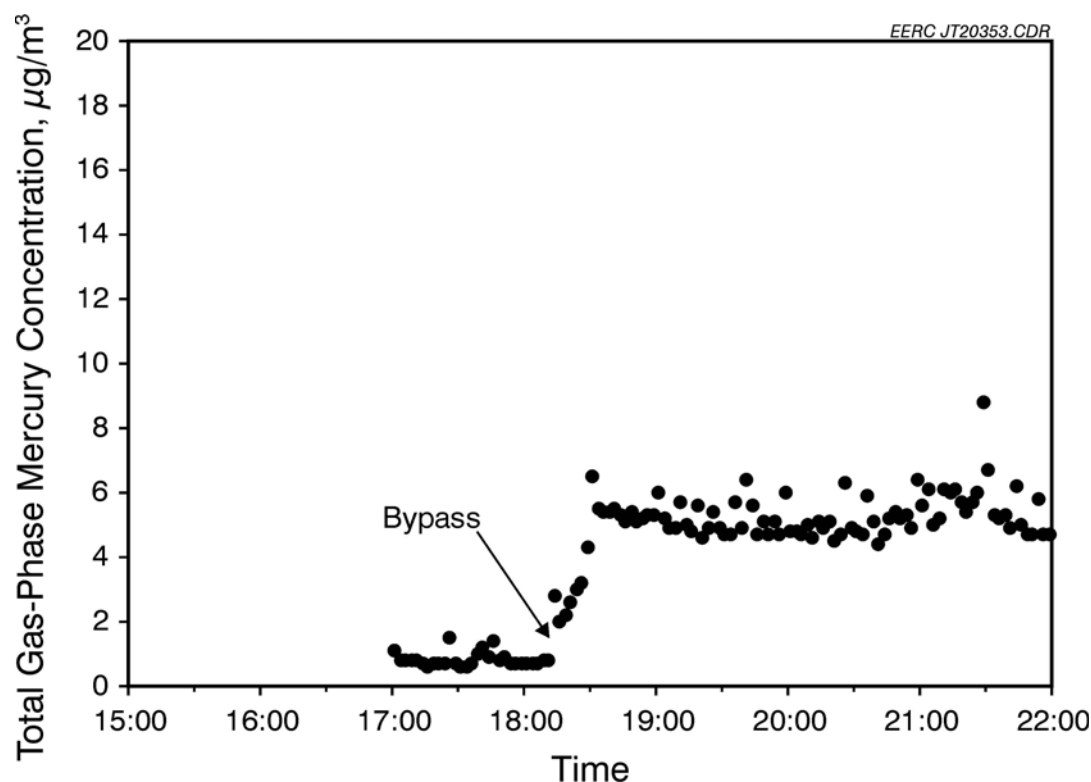


Figure 18. CMM data showing the effect of bypassing the SCR reactor.

## Effect of SCR Catalyst Age on Hg Speciation

Flue gas monitoring was conducted over 3 consecutive years at two power plants (Sites S2 and S4) to evaluate the impact catalyst age had on Hg speciation. The concern was that the oxidation potential of an SCR catalyst could be reduced with time. The first tests were conducted after approximately 3.5 months of catalyst age at Site S2 and after about 5 months at Site S4. Follow-up testing was then conducted after two additional ozone seasons at each plant. Figures 19 and 20 show the results of the testing at these two sites.

It appeared that there was a decrease in Hg oxidation across the SCR catalyst by the second season, particularly for Site S4. However, this was not apparent following the third season. Although the plant indicated the coal was from the same mine, it is possible there may have been some difference in the coal fired during the tests conducted in 2001 and 2002. The chlorine content was somewhat lower and the Hg concentration a little bit higher in 2002. Although there may have been some differences in the oxidation across the SCR catalyst, there was no significant difference at the inlet to the particulate control device at either site from the first season to the third.

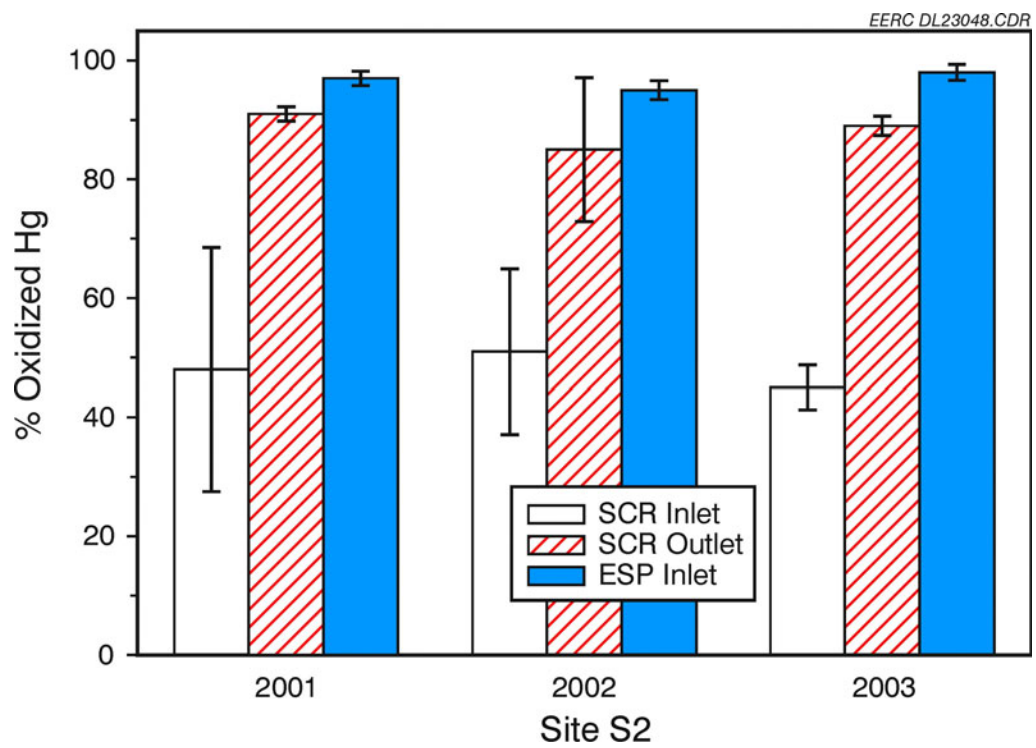


Figure 19. Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S2.

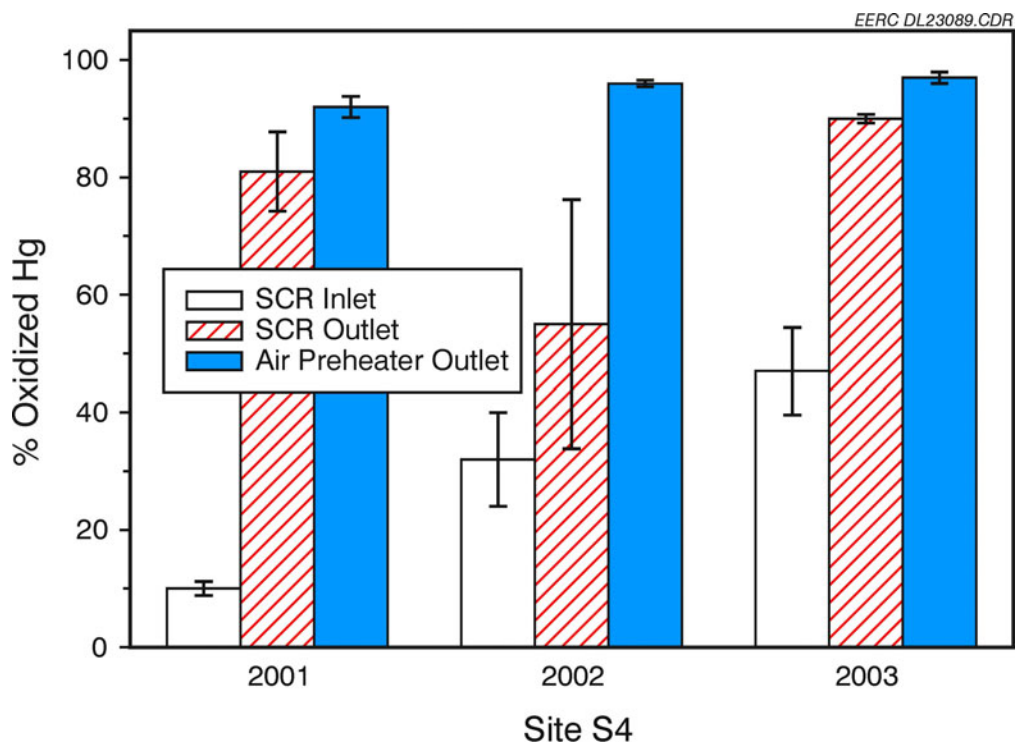


Figure 20. Comparison of Hg speciation results from 2001, 2002, and 2003 at Site S4.

## SCR/Wet FGD Combination for Hg Control

The underlying intent of understanding Hg oxidation via SCR technology is to determine its potential to improve the Hg collection efficiency of existing ESPs, fabric filters, and FGD systems in particular. In general, wet FGD systems remove more than 90% of  $\text{Hg}^{2+}$ . There has been evidence, however, that some of the captured  $\text{Hg}^{2+}$  can be reduced in the wet FGD system to  $\text{Hg}^0$ . [11, 18] Three sites have been tested that have wet FGD systems. Sites S2 and S5 employ magnesium-enhanced lime FGDs, and Site S4 is a combined particulate- $\text{SO}_2$  venturi-spray tower scrubber. It is important to note that approximately 60% of wet FGD systems in the United States are limestone forced-oxidation systems. As can be seen in Table 7, there is a measurable increase in  $\text{Hg}^0$  across the FGD unit at all of the sampling sites when SCR was not in service. For the tests with SCR in service, there was an increase in  $\text{Hg}^0$ , but the increase appears to be very small and is generally within the variability of the data. It should also be noted that there was little difference in the results each time Sites S2 and S4 were sampled, again indicating the catalyst age does not appear to effect Hg speciation and overall Hg removal.

Table 7. Effect of the SCR on  $\text{Hg}^0$  Concentration Across Wet FGDs

Site	Year Sampled	FGD Inlet $\text{Hg}^0$ Conc., $\mu\text{g}/\text{Nm}^3$	FGD Outlet $\text{Hg}^0$ Conc., $\mu\text{g}/\text{Nm}^3$	$\text{Hg}^0$ Increase <sup>a</sup> , $\mu\text{g}/\text{Nm}^3$	Total Hg Removed, %
<i>With SCR</i>					
S2	2001	0.4±0.2 <sup>b</sup>	0.9±0.1	0.5	89
S2	2002	0.3±0.2	1.3±0.2	1.0	84
S2	2003	0.3±0.1	0.6±0.2	0.3	90
S4	2001	1.0±0.4	1.3±0.3	0.3	91
S4	2002	0.5±0.1	0.8±0.1	0.3	90
S4	2003	0.3±0.1	0.4±0.1	0.1	91
S5	2002	0.7±0.2	1.0±0.3	0.3	91
<i>Without SCR</i>					
S2	2001	3.4±0.1 <sup>b</sup>	5.0±1.0	1.6	51
S4	2001	5.6±1.0	7.1±0.2	1.5	46
S4	2002	5.7±0.6	8.0±1.3	2.3	44
S5	2002	4.7±1.0	6.1±0.6	1.4	51

<sup>a</sup> Defined as (FGD outlet  $\text{Hg}^0$  conc. - FGD inlet  $\text{Hg}^0$  conc.).

<sup>b</sup> The ESP inlet data were used for site S2 in 2001 because FGD inlet Hg concentration values are clear outliers.

The mechanism for FGD reemission is not well understood, but it is speculated that sulfite in the FGD slurry may reduce  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ . The impact of forced oxidation may alter the sulfite chemistry, potentially giving different results than those obtained for the plants shown in Table 7. Because the mechanism of reemission is not well understood and it is not known how SCR units may impact reemission, the reader is cautioned in attempting to extrapolate the results from these three sites to all FGD systems. Additional studies are recommended and planned at plants with limestone forced-oxidation FGD systems.





## Conclusions

For plants firing eastern bituminous coals, Hg oxidation occurs across SCR catalysts. However, it appears to be variable and most likely related to a variety of factors. Some potential factors are coal characteristics; catalyst chemistry, structure, and age; and space velocity.

It appears that addition of an SCR unit, when an eastern bituminous coal is fired, will provide additional  $\text{Hg}^{2+}$ . With the exception of Sites S3 and S6 (where the Hg was essentially all  $\text{Hg}^{2+}$  or  $\text{Hg}_p$  both with and without SCR), all facilities showed increased oxidation at the inlet to the particulate control device. The increase ranged from 15 to 39 percentage points.

At both sites where sampling was done over a 3-year period, it appeared there was a decrease in Hg oxidation across the SCR catalyst between the first and second season, particularly for Site S4. However, this was not apparent following the third season. In addition, the overall mercury removal was the same for all 3 years. Although the plant personnel at Site S4 indicated the coal was from the same mine, it is possible there may have been some difference in the coal fired during the tests conducted in 2001 and 2002. The chlorine content was somewhat lower and the Hg concentration a little bit higher in 2002. Although there may have been some differences in the oxidation across the SCR catalyst, at the inlet to the particulate control device, there was no significant difference at either site from the first season to the third.

Based on the limited data at three plants, it appears there is some reemission of the captured Hg 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, at all three plants (over all three ozone seasons for Sites S2 and S4), there was an increase in  $\text{Hg}^0$ . When an SCR unit is not present, it appears that the reemission is more pronounced.

At two of the sites where flue gas conditioning agents were used to enhance ESP performance, it appeared that  $\text{NH}_3$  injection tended to increase  $\text{Hg}_p$  but inhibit Hg oxidation. However, at Site A2 where urea was injected into the boiler (SNCR), this was not the case. Therefore, it must be stressed that these are very limited tests, and the results are quite

variable.

When different blends of a PRB and eastern bituminous coal were fired, the results showed there was a decrease in  $Hg_p$  and an increase in  $Hg^0$  with increasing amounts of PRB.

## REFERENCES

1. U.S. Environmental Protection Agency. *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Final Report to Congress*, EPA/453/R-98/004A [NTIS PB98-131774]; Office of Air Quality Planning and Standards and Office of Research and Development, Executive Summary, Feb 1998.
2. Proposed National Emission Standards for Hazardous Air Pollutants; and, in the Alternative, Proposed Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units. 40 CFR Part 60 and 40 CFR Part 63, *Fed. Reg.*; 69, No. 20 4652–4752, 2004.
3. EPRI. *An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants*; EPRI Report No. 1000608, Oct 2000.
4. Hargrove, O.W. Jr.; Peterson, J.R.; Seeger, D.M.; Skarupa, R.C.; Moser, R.E. Update of EPRI Wet FGD Pilot-Scale Mercury Emissions Control Research. Presented at the EPRI–DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, ON, Canada, Aug 1995.
5. Holmes, M.J.; Redinger, K.E.; Evans, A.P.; Nolan, P.S. Control of Mercury in Conventional Flue Gas Emissions Control Systems. Presented at the Managing Hazardous Air Pollutants 4th International Conference, Washington, DC, Nov 12–14, 1997.
6. Information Collection Request Reports. <http://www.epa.gov/ttn/uatw/combust/utilttox/utoxpg.html> (accessed Oct 7, 2000).
7. Cichanowicz, J.E. Muzio, L.J. Factors Affecting Selection of a Catalyst Management Strategy. In *Proceedings of the Combined Power Plant Air Pollutant Control Mega Symposium*; Washington, DC, May 2003.
8. Gutberlet, H.; Schlöten, A.; Lienta, A. SCR Impacts on Mercury Emissions on Coal-Fired Boilers. Presented at the EPRI SCR Workshop, Memphis, TN, April 2000.
9. EPRI. *Pilot-Scale Screening Evaluation of the Impact of Selective Catalytic Reduction for NO<sub>x</sub> on Mercury Speciation*, EPRI Report No. 1000755, EPRI, Palo Alto, CA, 2000.
10. EPRI. *Power Plant Evaluation of the Effect of Selective Catalytic Reduction on Mercury*, EPRI Report No. 1005400, EPRI, Palo Alto, CA, 2002.
11. U.S. Environmental Protection Agency. *Effect of Selective Catalytic Reduction on Mercury, 2002 Field Studies Update*, EPA-600/R-04/032, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC: April 2004.
12. Miller, S.J.; Dunham, G.E.; Olson, E.S. Controlling Mechanisms That Determine Mercury Sorbent Effectiveness, Paper No. 99-898. Presented at the 92nd Annual Meeting & Exhibition of the Air & Waste Management Association, St. Louis, MO, June 1999.
13. Shashkov, V.I.; Mukhlenov, I.P.; Be\_yash, E.Y.; Ostanina, V.I.; Shokarev, M.M.; Vershinina, F.I. Effect of Mercury Vapors on the Oxidation of Sulfur Dioxide in a

- Fluidized Bed of Vanadium Catalyst. *Khim. Prom.* (Moscow); 47, 288–290, 1971.
14. Carey, T.R.; Skarupa, R.C.; Hargrove, O.W. Jr. *Enhanced Control of Mercury and Other HAPs by Innovative Modifications to Wet FGD Processes*; Phase I Report for U.S. Department of Energy Contract No. DE-AC22-95PC95260; Aug 28, 1988.
  15. Hitchcock, H.L. Mercury Sorption on Metal Oxides. M.S. Thesis, University of North Dakota; 83 p, Dec 1996.
  16. Galbreath, K.C.; Zygarlicke, C.J. Mercury Transformations in Coal Combustion Flue Gas. *Fuel Process. Technol.*, 65–66, 289–310, 2000.
  17. Ghorishi, S.B.; Lee, C.W.; Kilgroe, J.D. Mercury Speciation in Combustion Systems: Studies with Simulated Flue Gases and Model Fly Ashes. Presented at the 92nd Annual Meeting & Exhibition of the Air & Waste Management Association, St. Louis, MO, June 1999.
  18. Nolan, P.; Redinger, K.; Amrhein, G.; Kudlac, G. Mercury Emissions Control in Wet FGD Systems. Presented at the International Conference on Air Quality III: Mercury, Trace Elements, and Particulate Matter, Arlington, VA, Sept 9–12, 2002.

## **BIBLIOGRAPHY OF REPORTS COMPLETED FOR THIS PROJECT**

1. EPRI. *Pilot-Scale Screening Evaluation of the Impact of Selective Catalytic Reduction for NO<sub>x</sub> on Mercury Speciation*, EPRI Report No. 1000755, EPRI, Palo Alto, CA, 2000.
2. EPRI. *Power Plant Evaluation of the Effect of Selective Catalytic Reduction on Mercury*, EPRI Report No. 1005400, EPRI, Palo Alto, CA, 2002.
3. U.S. Environmental Protection Agency. *Effect of Selective Catalytic Reduction on Mercury, 2002 Field Studies Update*, EPA-600/R-04/032, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC: April 2004.
4. Interim Reports for Sites S8, S9, A4, and the third-year sampling at Site S2. These reports are in publication, but copies have been provided to the U.S. Department of Energy, EPRI, U.S. Environmental Protection Agency, and specific power plants.

TECHNICAL REPORT DATA			
(Please read Instructions on the reverse before completing)			
1. REPORT NO. <b>EPA-600/R-04/147</b>		2.	
4. TITLE AND SUBTITLE <b>Selective Catalytic Reduction Mercury Field Sampling Project</b>		3. RECIPIENT'S ACCESSION NO.	
		5. REPORT DATE <b>November 2004</b>	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHORS <b>Dennis L. Laudal, Jeffrey S. Thompson, Chad A. Wocken (EERC, U. of North Dakota)</b>		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Energy &amp; Environmental Research Center University of North Dakota PO Box 9018 Grand Forks, ND 58202-9018</b>		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. <b>R 83060601</b>	
12. SPONSORING AGENCY NAME AND ADDRESS <b>U. S. EPA, Office of Research and Development Air Pollution Prevention and Control Division Research Triangle Park, North Carolina 27711</b>		13. TYPE OF REPORT AND PERIOD COVERED <b>Final Summary; 03/01/01-06/30/04</b>	
		14. SPONSORING AGENCY CODE <b>EPA/600/13</b>	
15. SUPPLEMENTARY NOTES <b>The EPA Project Officer is Chun Wai Lee, Mail Drop E305-01, phone (919) 541-7663, e-mail lee.chun-wai@epamail.epa.gov.</b>			
16. ABSTRACT <b>The report provides a summary of the testing of the Selective Catalytic Reduction Mercury Field Sampling Project. The electric utility industry is investigating methods to control and reduce mercury (Hg) emissions because EPA proposed in 2000 to regulate Hg emissions from coal-fired power plants. The project investigated the impact of selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), flue gas-conditioning systems, and coal blending on speciation and capture of Hg from coal-fired electric utility boilers. The results indicate that SCR can assist in converting elemental Hg to an oxidized form. However, the effect appears to be coal-specific and, possibly, catalyst-specific. Significant increase in Hg oxidation across the SCR reactor was observed for plants firing an eastern bituminous coal. The two plants that showed very little increase in oxidation across the SCR fired Power River Basin subbituminous coal; results of the repeated tests for the two plants show very little aging effect of the SCR catalyst for reducing Hg oxidation over a 3-year period. Ammonia-based flue gas conditioning agents, whether injected directly as NH<sub>3</sub> gas or indirectly as NH<sub>2</sub>CONH<sub>2</sub> and NH<sub>4</sub>HSO<sub>4</sub>, did not appear to have a significant effect on Hg speciation and removal. Results of the coal blending tests show significant increase of particulate-bound Hg and decrease of Hg<sup>0</sup> with increasing amounts of bituminous coal in the coal blends.</b>			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Electric Power Plants Boilers Coal Combustion Emission Flue Gases		Pollution Control Stationary Sources	13B 07B 10B 13A 06E 21D 21B 14G
18. DISTRIBUTION STATEMENT  <b>Release to Public</b>		19. SECURITY CLASS (This Report) <b>Unclassified</b>	21. NO. OF PAGES <b>60</b>
		20. SECURITY CLASS (This Page) <b>Unclassified</b>	22. PRICE