Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Fuels

Quarterly Progress Report

Reporting Period Start Date January 1, 2004
Reporting Period End Date: March 31, 2004

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April 30, 2004

DOE Cooperative Agreement No: DE- FC26-03NT41728

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Abstract

This is the fifth Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-03NT41728. The objective of this program is to measure the oxidation of mercury in flue gas across SCR catalyst in a coal-fired power plant burning low rank fuels using a slipstream reactor containing multiple commercial catalysts in parallel. The Electric Power Research Institute (EPRI) and Argillon GmbH are providing co-funding for this program. This program contains multiple tasks and good progress is being made on all fronts. During this quarter, the available data from laboratory, pilot and full-scale SCR units was reviewed, leading to hypotheses about the mechanism for mercury oxidation by SCR catalysts.

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Executive Summary

This project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-03NT41728. The Electric Power Research Institute (EPRI) and Argillon GmbH are providing co-funding for this program. This project has a period of performance that started February 19, 2003 and continues through September 30, 2004.

Under a separate program (cooperative agreement DE-FC26-00NT40753), Reaction Engineering International (REI) has been funded by the Department of Energy to carry out research and development on NO_x control options for coal-fired utility boilers. The objective of one of the tasks in the NO_x-control program is to evaluate and model SCR catalyst deactivation. REI will be responsible for six-month testing of multiple commercial catalysts simultaneously in a power plant slipstream reactor. This multi-catalyst reactor provides an ideal test bed for advancing the state of knowledge regarding mercury oxidation by SCR catalysts, with a focus on low rank fuels.

In this program, REI is using the multi-catalyst slipstream reactor to determine oxidation of mercury across six separate SCR catalysts at AEP's Rockport Unit 1. During the six-month testing under the existing NO_x-control program, two week-long sampling campaigns for mercury speciation will be carried out: at the beginning of the six-month period and at an intermediate point. URS will conduct the one-week campaigns to measure gaseous mercury speciation at the inlet and at the outlet of each catalyst chamber.

The specific project tasks are:

- Task 1 Test Preparation
- Task 2 Test Plan
- Task 3 Field Measurements of Mercury Speciation
- Task 4 Data Analysis and Validation
- Task 5 Management and Reporting

During the last three months, our accomplishments included the following:

- Available data from laboratory, pilot and full-scale SCR units was reviewed, leading to hypotheses about the mechanism for mercury oxidation by SCR catalysts.

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Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the Tasks as outlined in our original proposal.

Task 4 - Data Analysis and Validation

Data have been collected from measurements of mercury speciation across SCR reactors in laboratory and pilot-scale experiments. The datasets collected are summarized in Table 1.

Table 1. SCR data sets, pilot and laboratory scale data.

Boiler Name	Unit 2	Unit 2	Unit 2
Reference	1	1	1
Scale	Pilot-scale	Pilot-scale	Pilot-scale
Boiler Capacity, MW	605	605	605
Boiler Type	R_Turbo type	R_Turbo type	R_Turbo type
SCR Catalyst Type	Ti/V based SCr catalyst installed as a single bed w/ depth of 1m	Ti/V based SCr catalyst installed as a single bed w/ depth of 1m	Ti/V based SCr catalyst installed as a single bed w/ depth of 1m
SCR Mfr			
SCR Space velocity, 1/hr		1458	
SCR Notes	slipstream Pilot scale SCR	slipstream Pilot scale SCR	slipstream Pilot scale SCR
Experiment Notes		Tests not carried out in presence of fly ash or continuous NH3 addition	
Experimental Study	Effect of Exposure time on Hg^0 Oxidation	Slipstream test: Effect of NH3 and Exposure time on Hg0 Oxidation	Hg^0 oxidation as function of NH3/Nox Molar Ratio
Coal Rank	PRB	PRB	PRB
FG Location:	sampling port downstream of catalyst in SCR	sampling port downstream of catalyst in SCR	sampling port downstream of catalyst in SCR
FG Type:	derived	derived	derived
FG Exposure Time (hrs)			1450
FG Temperature, F	700	700	700
FG O2 %			
FG CO2 %			
FG H2O %			
FG HCl, ppm, dry, 3% O2			
FG SO2, ppm, dry, 3% O2			
FG NOx, ppm, dry, 3% O2			
FG SO3, ppm, dry, 3% O2			
FG CO, ppm			
FG NH3, ppm, dry, 3% O2	$NH3/NO_x$ molar ratio=0.8		
Hg^0 Oxidation (% of Inlet)			
FG Hg[0], ug/dnm3 @3% O2			

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name	Unit 2		
Reference	2	2	2
Scale	Pilot-scale	Pilot scale- laboratory	Pilot scale- laboratory
Boiler Capacity, MW	605		
Boiler Type	R_Turbo type		
SCR Catalyst Type	Ti/V based SCr catalyst installed as a single bed w/ depth of 1m	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch
SCR Mfr			
SCR Space velocity, 1/hr			
SCR Notes	slipstream Pilot scale SCR	Fresh catalyst used: flue gas flowed across catalyst until adsorption equilibrium was attained. Hg^0 measurement then taken.	Fresh catalyst used: flue gas flowed across catalyst until adsorption equilibrium was attained. Hg^0 measurement then taken.
Experiment Notes			
Experimental Study	Effect of Space Velocity and NH_3 addition on Hg^0 Oxidation		
Coal Rank	PRB	PRB	eastern bituminous
FG Location:	sampling port downstream of catalyst in SCR		
FG Type:	derived	simulated	simulated
FG Exposure Time (hrs)	3200		
FG Temperature, F	700		
FG O2 %			5
FG CO2 %			12
FG H2O %			7
FG HCl, ppm, dry, 3% O2			50
FG SO2, ppm, dry, 3% O2			1600
FG NOx, ppm, dry, 3% O2			400
FG SO3, ppm, dry, 3% O2			
FG CO, ppm			
FG NH3, ppm, dry, 3% O2			0
Hg^0 Oxidation (% of Inlet)			98.5/ 95/ 91
FG Hg[0], ug/dnm3 @3% O2			20-40

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name			
Reference	2	2	2
Scale	Pilot scale- laboratory	Pilot scale- short-term slipstream tests	Pilot scale- short-term slipstream tests
Boiler Capacity, MW			
Boiler Type			
SCR Catalyst Type	Commercial Ti/V-based SCR catalyst; wash-coated honey comb with a 10-mm cell pitch	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Commercial Ti/V-based SCR catalyst; wash-coated honey comb with a 10-mm cell pitch
SCR Mfr			
SCR Space velocity, 1/hr			
SCR Notes	Fresh catalyst used: flue gas flowed across catalyst until adsorption equilibrium was attained. Hg0 measurement then taken.	Fresh catalyst used: flue gas flowed across catalyst until adsorption equilibrium was attained. Hg^0 measurement then taken.	Fresh catalyst used: flue gas flowed across catalyst until adsorption equilibrium was attained. Hg0 measurement then taken.
Experiment Notes		EPRI's mini catalyst test unit was used	EPRI's mini catalyst test unit was used
Experimental Study			
Coal Rank	PRB	PRB	PRB
FG Location:		catalyst outlet	
FG Type:	simulated	derived	derived
FG Exposure Time (hrs)			
FG Temperature, F			
FG O2 %			
FG CO2 %			
FG H2O %			
FG HCl, ppm, dry, 3% O2			
FG SO2, ppm, dry, 3% O2			
FG NOx, ppm, dry, 3% O2			
FG SO3, ppm, dry, 3% O2			
FG CO, ppm			
FG NH3, ppm, dry, 3% O2			
Hg^0 Oxidation (% of Inlet)			
FG Hg[0], ug/dnm3 @3% O2			

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name			
Reference	3 (Site 1)	3 (Site 2)	3 (Site 3)
Scale	Pilot scale- slipstream tests	Pilot scale- slipstream tests	Pilot scale- slipstream tests
Boiler Capacity, MW			
Boiler Type			
SCR Catalyst Type	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch
SCR Mfr			
SCR Space velocity, 1/hr		759/ 1109/ 2918/ 5097/ 14591	
SCR Notes			
Experiment Notes	Pilot SCR		
Experimental Study			
Coal Rank	PRB- pulverized coal	eastern bituminous- pulverized coal	Lignite
FG Location:	Pilot SCR Inlet	Air Heater Inlet	cold-side ESP outlet (flue gas was reheated)
FG Type:	derived	derived	derived
FG Exposure Time (hrs)			
FG Temperature, F			
FG O2 %			
FG CO2 %			
FG H2O %			
FG HCl, ppm, dry, 3% O2			
FG SO2, ppm, dry, 3% O2			
FG NOx, ppm, dry, 3% O2			
FG SO3, ppm, dry, 3% O2			
FG CO, ppm			
FG NH3, ppm, dry, 3% O2			
Hg^0 Oxidation (% of Inlet)			
FG Hg[0], ug/dnm3 @3% O2			

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name			
Reference	3 (Site 4)	3 (Site 4)	4
Scale	Full-scale	Full-scale	Pilot Scale- Laboratory
Boiler Capacity, MW	Cyclone	Cyclone	
Boiler Type			
SCR Catalyst Type	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Commercial Ti/V-based SCR catalyst; extruded honeycomb with a 10- mm cell pitch	Honey comb 35cells, pitch: 4.2mm; Geometric surface area: 0.6475 m2
SCR Mfr			Ceramics GmbH
SCR Space velocity, 1/hr	767/ 1401/ 2160/ 2724/ 5720/ 7879/ 9981	671/ 1626/ 2622/ 6870/ 13618	
SCR Notes			
Experiment Notes	Full scale SCR	Full scale SCR	
Experimental Study			
Coal Rank	PRB	PRB	bituminous coal
FG Location:	SCR Inlet and Outlet	SCR Inlet	downstream of catalyst
FG Type:	derived	derived	simulated
FG Exposure Time (hrs)			
FG Temperature, F			
FG O2 %			2.8
FG CO2 %			
FG H2O %			2.9
FG HCl, ppm, dry, 3% O2			61
FG SO2, ppm, dry, 3% O2			520
FG NOx, ppm, dry, 3% O2			432-450
FG SO3, ppm, dry, 3% O2			
FG CO, ppm			44
FG NH3, ppm, dry, 3% O2			Stoich ratio NO/NH3=1
Hg^0 Oxidation (% of Inlet)			
FG Hg[0], ug/dnm3 @3% O2			24.7-32.2

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name			
Reference	4	4	4
Scale	Pilot Scale- Laboratory	Pilot Scale- Laboratory	Pilot Scale- Laboratory
Boiler Capacity, MW			
Boiler Type			
SCR Catalyst Type	Honey comb 22cells, pitch: 6.7mm; Geometric surface area: 0.6496 m2	Plate-type, pitch: 6.3mm; Geometric surface area: 0.6480 m2	Empty Catalytic Unit
SCR Mfr	Ceramics GmbH	Ceramics GmbH	
SCR Space velocity, 1/hr			
SCR Notes			
Experiment Notes			
Experimental Study			
Coal Rank	bituminous coal	bituminous coal	bituminous coal
FG Location:	downstream of catalyst	downstream of catalyst	downstream of catalyst
FG Type:	simulated	simulated	simulated
FG Exposure Time (hrs)			
FG Temperature, F	284/ 326/ 330/ 382/ 405 °C	278/ 325/ 380/ 410 °C	280/ 288/ 333/ 372/ 400
FG O2 %	2.74-2.82	2.8	2.74
FG CO2 %			
FG H2O %	2.9-3.0	3	2.8
FG HCl, ppm, dry, 3% O2	62	62	59
FG SO2, ppm, dry, 3% O2	522-538	529	506
FG NOx, ppm, dry, 3% O2	522-532	430	506-520
FG SO3, ppm, dry, 3% O2			
FG CO, ppm	53	45	66
FG NH3, ppm, dry, 3% O2	Stoich ratio NO/NH3=1	Stoich ratio NO/NH3=1	Stoich ratio NO/NH3=1
Hg^0 Oxidation (% of Inlet)	68/ 77/ 80/ 81/ 84	87/ 88/ 82/ 78	6/ 6/ 18/ 9/ 12
FG Hg[0], ug/dnm3 @3% O2	14.6-26.4	18.4-23.5	20.3-40.5

Table 1 [continued]. SCR data sets, pilot and laboratory scale data.

Boiler Name			
Reference	4	4	4
Scale	Pilot Scale- Laboratory	Pilot Scale- Laboratory	Pilot Scale- Laboratory
Boiler Capacity, MW			
Boiler Type			
SCR Catalyst Type	Plate-type, pitch: 6.3mm; Geometric surface area: 0.6480 m2	Plate-type, pitch: 6.3mm; Geometric surface area: 0.6480 m2	Plate-type, pitch: 6.3mm; Geometric surface area: 0.6480 m2
SCR Mfr	Ceramics GmbH	Ceramics GmbH	Ceramics GmbH
SCR Space velocity, 1/hr			
SCR Notes			
Experiment Notes			
Experimental Study			
Coal Rank	bituminous coal	bituminous coal	bituminous coal
FG Location:	downstream of catalyst	downstream of 2nd layer	downstream of 1st layer
FG Type:	simulated	simulated	simulated
FG Exposure Time (hrs)			
FG Temperature, F	292/ 322/ 380/ 410 °C	292/ 322/ 380/ 410 °C	292/ 322/ 380/ 410 °C
FG O2 %	2.77-2.88	2.77-2.88	2.77-2.88
FG CO2 %			
FG H2O %	2.9-3.0	2.9-3.0	2.9-3.0
FG HCl, ppm, dry, 3% O2	10	10	10
FG SO2, ppm, dry, 3% O2	524-544	524-544	524-544
FG NOx, ppm, dry, 3% O2	395-410	395-410	395-410
FG SO3, ppm, dry, 3% O2			
FG CO, ppm	38	38	38
FG NH3, ppm, dry, 3% O2	Stoich ratio NO/NH3=1	Stoich ratio NO/NH3=1	Stoich ratio NO/NH3=1
Hg^0 Oxidation (% of Inlet)	76/ 72/ 68/ 47	47/ 52/ 45/ 27	10/ 16/ 17/ 12
FG Hg[0], ug/dnm3 @3% O2	14.9-19.2	14.9-19.2	14.9-19.2

Results and Discussion

Task 4 - Data Analysis and Validation

We get some picture of the processes that are taking place in the SCR, starting with an examination of laboratory data and then looking at pilot and full-scale data for corroboration.

Elemental mercury is adsorbed by the catalyst until some steady state is reached [5,6]. The amount of mercury adsorbed appears to be related to the HCl content of the flue gas in laboratory experiments carried out by Hocquel and coworkers with commercial catalyst. In Figure 1, reproduced from Reference 6, mercury was measured at the inlet and outlet of commercial catalysts where a simulated flue gas containing varying levels of HCl was passed through the catalyst for ten minutes. At high concentrations (~20 to 75 ppm) of HCl, the outlet mercury concentration was almost equal to the inlet mercury. At low concentrations (~0.2 to 2 ppm) of HCl, however, the catalyst initially adsorbed 80 to 90 percent of the incoming mercury.

The

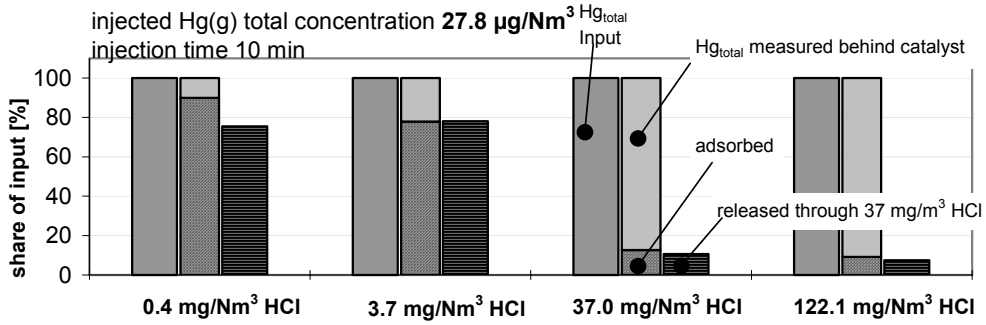


Figure 1. Influence of HCl concentration on mercury adsorption across SCR catalyst using simulated flue gas. [Reproduced from Reference 6]

presence of HCl therefore reduced the amount of mercury adsorbed on the catalyst. Transient experiments in the same laboratory showed that a step increase in the HCl concentration caused an increase in mercury exiting the catalyst in concentrations above the inlet level of mercury [2] as illustrated in Figure 2.

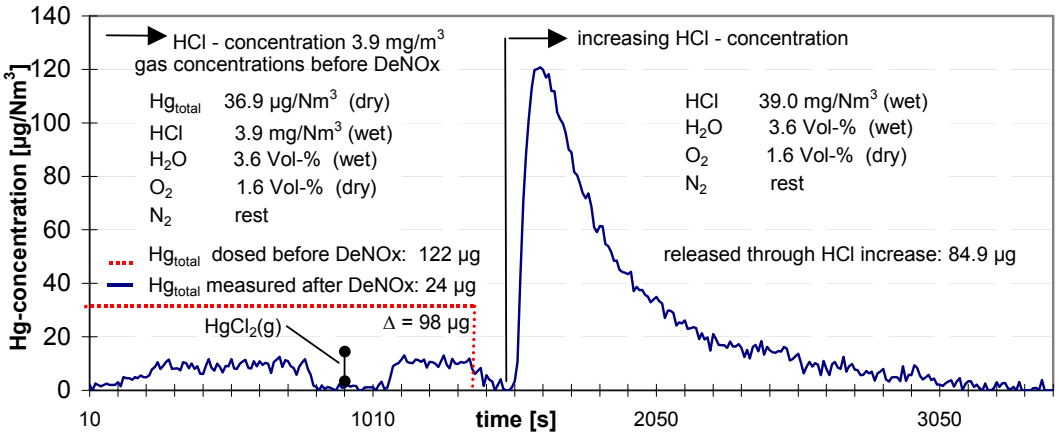


Figure 2. Time response of mercury adsorption and release of SCR catalyst. [taken from Reference 6]

Laboratory experiements by Lee and co-workers [5] demonstrated that when HCl and Hg^0 (in a simulated flue gas mixture) were present in the gas entering the SCR reactor, oxidized mercury exited the reactor, but when there was no HCl in the same simulated flue gas, very little oxidized mercury was formed at the outlet, suggesting that HCl reacted with the adsorbed mercury, prompting it to desorb. At this point, we do not know if there is a direct reaction between adsorbed elemental mercury and HCl, or if there is an intermediate like HgO formed on the surface and then subsequently oxidized.

Experiments by Hocquel et al. [7] show the effect of HCl concentration in simulated flue gas on the amount of $HgCl_2$ exiting a laboratory SCR reactor, with and without SO_2 present (Figure 3). HCl concentration had a major impact on the amount of $HgCl_2$ exiting the catalyst. Several

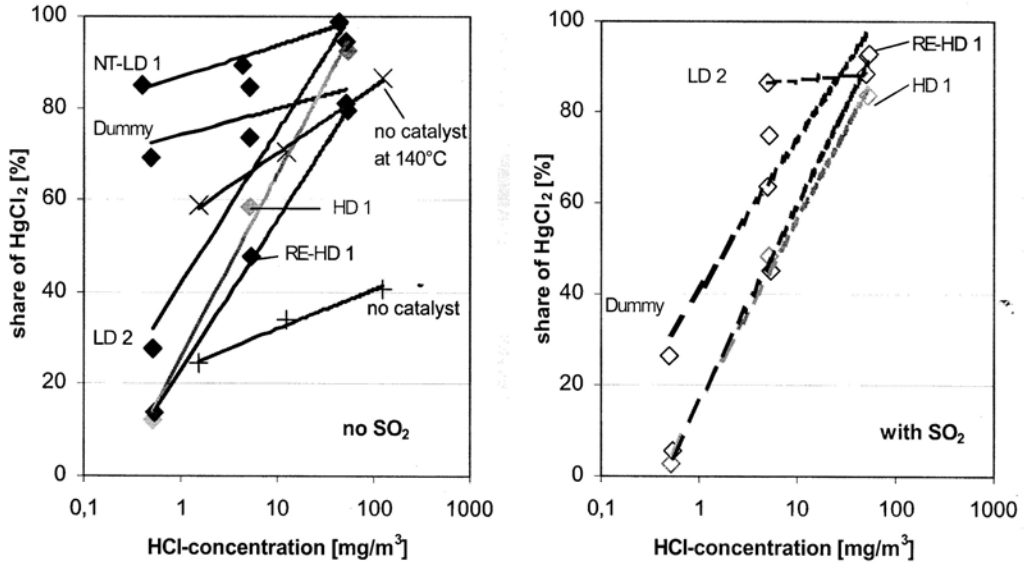


Figure 3. Percentage of $HgCl_2$ exiting SCR catalysts at 330°C (625°F) for simulated flue gas mixtures containing 1.7-1.85% O_2, 2.9-4% H_2O, 20 µg/m³ Hg, variable HCl and SO_2. [Reproduced from Reference 7].

different types of catalysts were tested and the figure shows that the type of catalyst affected the oxidation of Hg^0 via HCl. This may due to differences in pore structure among different catalysts as well as the concentrations of different metal oxides (V, W, Mo) in the catalyst. SO_2 had a minor impact on mercury oxidation in these experiments.

Transient experiments in the slipstream reactor at Rockport have shown that a step increase in ammonia (when the ammonia is turned on, for example) caused an increase in mercury exiting the catalyst, suggesting that ammonia can displace mercury from sites on the catalyst (Figure 4). Lee et al. [5] also noted in their laboratory experiments with simulated flue gas that when Hg^0 was first admitted to an SCR catalyst very little was measured at the outlet. However, when ammonia was subsequently added to the reactor, Hg^0 was measured at the outlet of the catalyst.

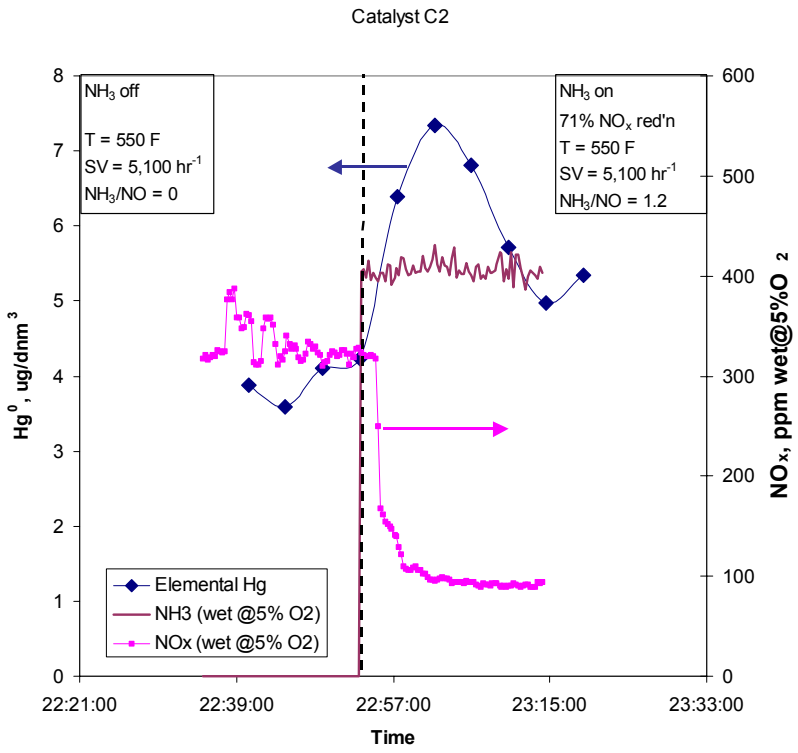


Figure 4. Elemental mercury and NO_x as a function of time for catalyst C2; T=550 F, SV=5,100 hr^{-1}.

Laboratory experiments using three layers of commercial monolith catalyst, in which mercury oxidation was measured in between layers, show the effect of ammonia on mercury oxidation [4]. As the NO_x was reduced along the length of the reactor, ammonia was consumed. Thus the first layer of the catalyst would have a higher concentration of ammonia than the second layer. Figure 5 shows the incremental mercury oxidation across each layer in this laboratory experiment. The first layer (with the highest ammonia concentration) showed the lowest mercury oxidation. The second and third layers, showed higher oxidation.

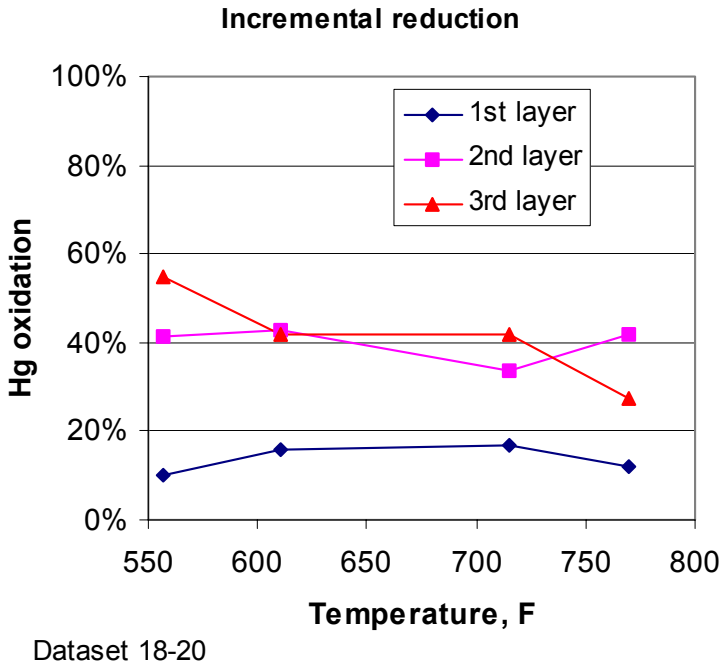


Figure 5. Mercury oxidation per layer of catalyst as a function of temperature. Space velocity 4800 to 5600 hr^{-1} for simulated flue gas mixtures containing 2.8-12.9% O_2, 2.9-3% H_2O, 395-410 ppm NO, 524-544 ppm SO_2, 10 ppm HCl, 38 ppm CO, 15-19 µg/m^3 Hg,, NH_3/NO=1 [Data from Reference 4]

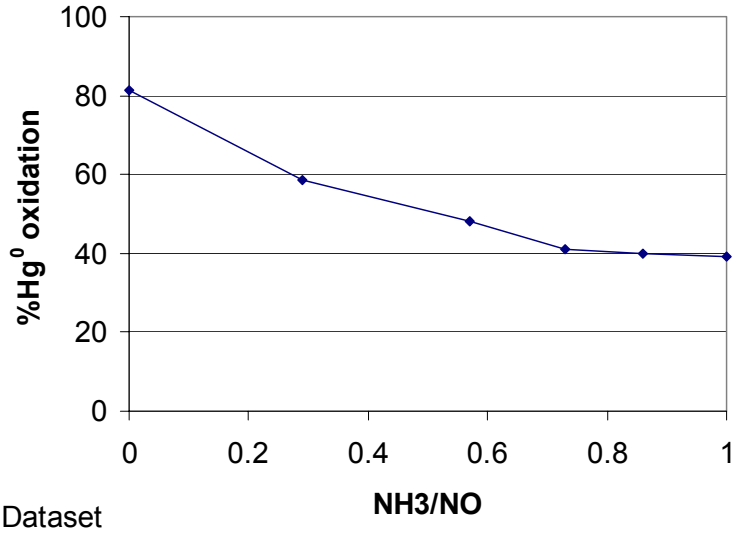


Figure 6. Mercury oxidation in slipstream reactor with PRB flue gas as a function of NH_3/NO ratio. [Data from Reference 1]

Further evidence of the effect of ammonia can be seen from slipstream experiments conducted at Pleasant Prairie power plant by URS using a one-meter length of catalyst. The flue gas is from a Powder River Basin (PRB) subbituminous coal that is low in HCl. Figure 6 shows the effect of NH_3/NO ratio on mercury oxidation across the catalyst. With no ammonia, 80 percent oxidation was observed. As the ammonia concentration was increased the mercury oxidation decreased. There was little effect on mercury oxidation for NH_3/NO ratios greater than 0.7.

Since it is known that ammonia adsorbs on metal oxide sites on the catalyst, this suggests that mercury (elemental or perhaps HgO) may be bound to one of the same active sites that bind ammonia (probably vanadium oxide but other metal oxides may be involved as well). There are not enough laboratory experiments on the effect of SO_2 or SO_3 on mercury oxidation by SCR catalysts. The effects of HCl and ammonia seem clear enough and can also be seen in the results of pilot and full-scale measurements.

Measurements of mercury oxidation have been carried out using a slipstream reactor and ash-free flue gas, either simulated flue gas or flue gas taken from a full-scale power plant [1-3]. These results

demonstrate the effects of temperature, space velocity, ammonia and flue gas composition.

Table 2. Simulated flue gas compositions used in experiments in Reference 2.

	Simulated PRB	Simulated Bituminous
SO_2	400 ppm	1600 ppm
HCl	2 ppm	50 ppm
NO_x	400 ppm	400 ppm
H_2O	7 %	7 %
CO_2	12 %	12 %
O_2	5%	5%
Hg^0	20-40 µg/Nm^3	20-40 µg/Nm^3
N_2	Balance	Balance

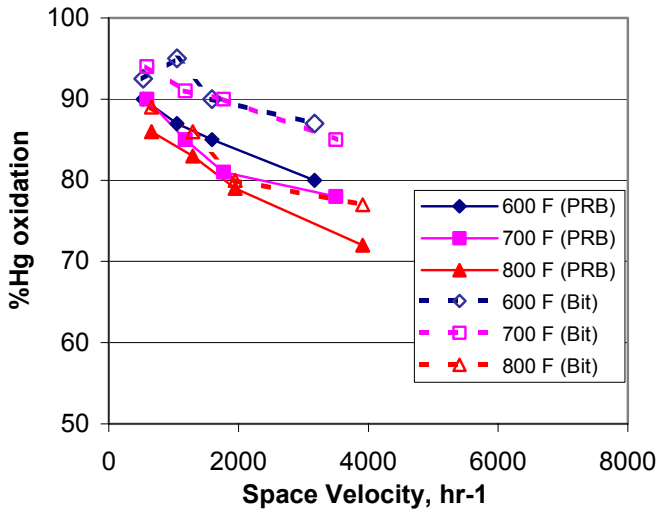
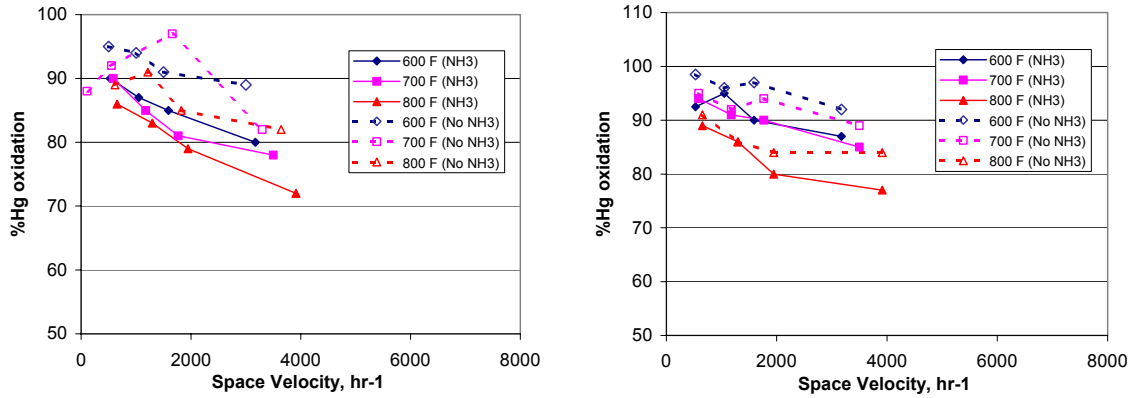


Figure 7. Mercury oxidation across SCR catalyst exposed to two different simulated flue gas mixtures with NH_3/NO=1 (see Table 2). [Reference 2]

Simulated flue gases (Table 2) were used with commercial Ti/V-based SCR catalyst; extruded honeycomb catalyst with a 10-mm cell pitch. The simulated PRB gas had lower HCl and SO_2 than the simulated bituminous gas. Figure 7 shows the measured mercury oxidation for one catalyst (an extruded monolith) with the different simulated flue gas compositions. The bituminous simulated flue gas produced higher mercury oxidation, as might be suspected from the higher HCl-content. Mercury oxidation increased as temperature decreased; the highest oxidation was at 600°F.

Under these conditions, two different catalysts, the extruded monolith and a wash-coated monolith were tested using the simulated PRB flue gas. For this gas composition, the two catalysts produced very similar mercury oxidation as a function of temperature and space velocity.

Without ammonia in the simulated flue gas mixture, the mercury oxidation increased for both the simulated bituminous and PRB flue gas composi-tions (Figure 8).

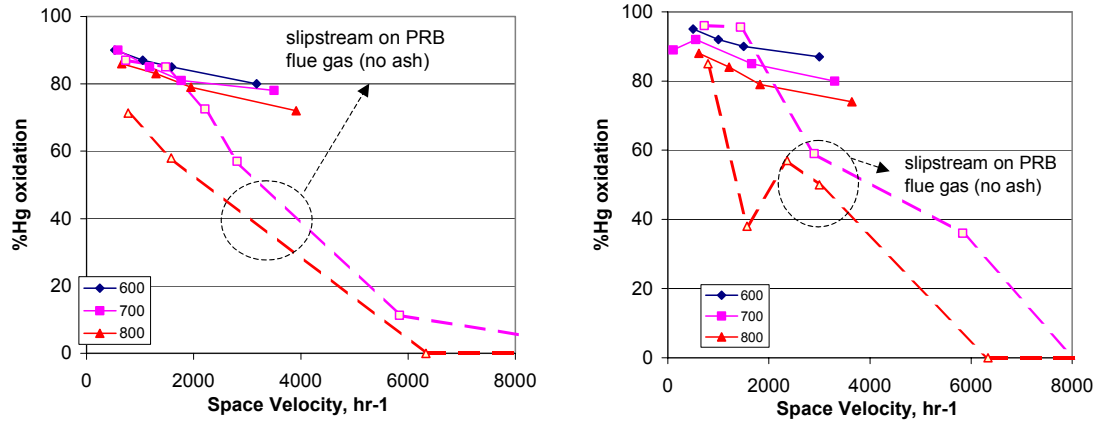


(a) Dataset 5 - Catalyst C1 with PRB flue gas

(b) Dataset 6 - Catalyst C1 with bituminous flue gas

Figure 8. Mercury oxidation of extruded monolith catalyst as function of temperature and space velocity with (NH_3/NO=1) and without ammonia for (a) PRB composition gas and (b) eastern bituminous gas composition. [Reference 2]

Simulated flue gas does not always produce mercury oxidation behavior that is consistent with that observed in flue gases derived from full-scale power plants. Further work by URS has been carried out on using flue gas from full-scale power plants instead of simulated flue gas. Figure 9 compares the extruded and wash-coated catalysts with the simulated PRB flue gas (Table 2) and flue gas from the Pleasant Prairie power plant [1], which burns a PRB coal. The Pleasant Prairie flue gas is ash-free. There are differences in the levels of mercury oxidation at a given space velocity between simulated and actual flue gas; furthermore the dependence of oxidation on



(a) NH_3/NO=1, Catalyst

(b), NH_3/NO=1, Catalyst 2

Figure 9. Mercury oxidation of monolith catalysts as function of temperature and space velocity with (NH_3/NO=1) for ash-free, simulated flue gas [2] and actual flue gas [1] for (a) extruded monolith and (b) wash-coated monolith.

space velocity is fundamentally different between simulated and actual flue gas, suggesting that there are components in the actual flue gas that may interfere with mercury adsorption or oxidation at higher space velocities (shorter residence times), perhaps because of competition for active sites.

The effect of ash deposits on SCR catalysts cannot be neglected, particularly high calcium ash deposits. CaO has been demonstrated, in laboratory experiments [7], to reduce $HgCl_2$ back to Hg^0. In simulated flue gas mixtures, the presence of both SO_2 and solid CaO in the gas resulted in greater amounts of incoming $HgCl_2$ being converted to Hg^0 at temperatures above 400 K (127°C or 260°F); the conversion of Hg^0 to $HgCl_2$ increased with increasing temperature [8]. On the other hand, $HgCl_2$ sorption by CaO (no SO_2 present) decreased with increasing temperature; adsorption was 45% at 420 K (150°C or 300°F), but fell to zero at 570 K (300°C or 565°F). The concentration of HCl in the gas-phase did not have an effect on either adsorption or conversion of $HgCl_2$ to Hg^0. This suggests that fly ash containing significant amounts of CaO might convert $HgCl_2$ to Hg^0 at temperatures characteristic of the SCR, but not at ESP or scrubber temperatures. Thus, high-calcium ash in SCR catalysts on units burning PRB coals might contribute to an apparent low amount of oxidation of Hg^0 to $HgCl_2$.

The slipstream reactor in this program that was deployed at AEP's Rockport plant did have ash in the SCR catalysts; the plant burned a blend of PRB and bituminous coal, giving about five times higher HCl concentrations that would be expected with a PRB coal alone. In Figure 10, the observed mercury oxidation from the March/April measurement campaign at the Rockport plant is compared with URS's slipstream data on a single catalyst (the extruded honeycomb) tested at three different full-scale power plants in the slipstream reactor (ash-free). The Rockport data fall between the Eastern bituminous and PRB cyclone curves and generally follow the same trend of mercury oxidation with space velocity as observed in the URS measurements. Catalysts C2 and C4 from the Rockport tests have higher oxidation, more similar to the PRB cyclone data, while catalysts C3, C5 and C6 show oxidation behavior more similar to the PRB PC-fired data.

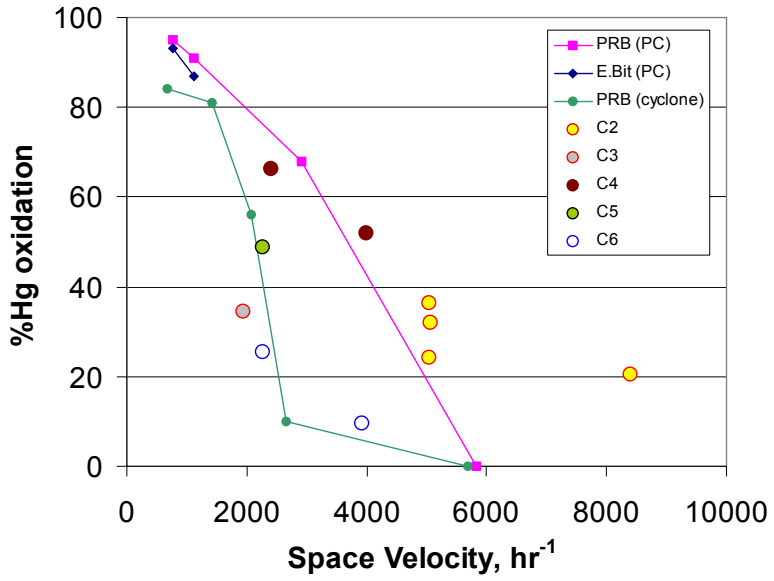


Figure 10. Mercury oxidation as a function of space velocity for URS ash-free slipstream data [8] at 700°F with ammonia, shown in with solid lines, and Rockport slipstream reactor data from March 2003.

Laboratory and pilot data show the effects of temperature, space velocity, flue gas composition and ammonia on mercury oxidation. In full-scale SCRs, it is not possible to make large changes in space velocity or temperature. However, flue gas composition (coal composition) and ammonia can be changed. In the previous quarterly report, the

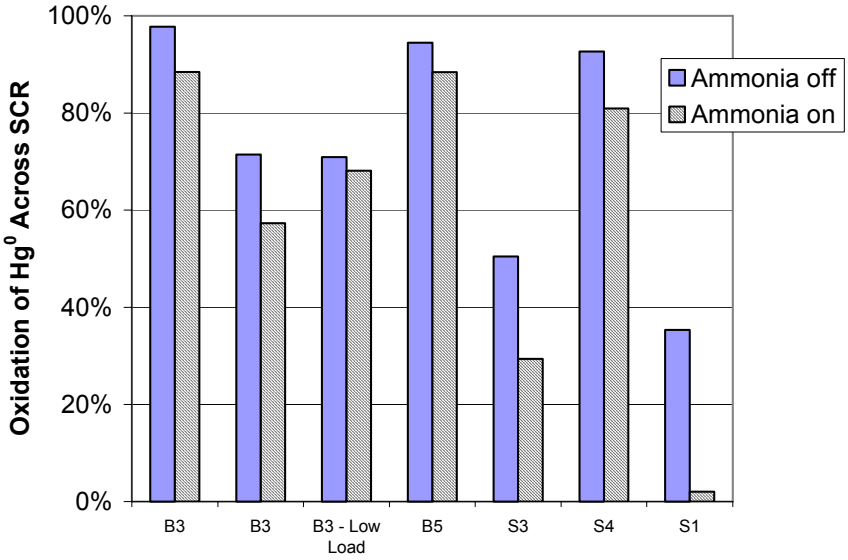


Figure 11. Mercury oxidation across full-scale SCRs with and without ammonia for different plants.

available full-scale datasets were summarized. Figure 11 shows mercury oxidation data from four full-scale power plants burning bituminous coals and one burning a PRB coal in a cyclone boiler, with and without ammonia on. The bituminous plants show mercury oxidation from 50 percent up to 98 percent without ammonia and from 30 percent to 90 percent with ammonia on. S1, the single PRB plant, however, shows only 35 percent oxidation without ammonia and about 4 percent oxidation with ammonia. This mirrors the trends seen in laboratory and pilot-scale data: low HCl in the flow gas results in lower mercury oxidation and the presence of ammonia decreases the amount of mercury oxidation.

In laboratory experiments the effect of HCl concentration on mercury oxidation was observed to be very pronounced; this was supported indirectly by pilot-scale data using mixtures of simulated flue gas and flue gas from full-scale power plants. Figure 12 displays the mercury oxidation from full-scale SCRs as a function of coal chlorine content. The range of data observed for the Rockport slipstream reactor is also shown on the figure. The full-scale data have been divided into low- and high-sulfur, to see if the sulfur content of the coal appears to have an effect on mercury oxidation. The figure suggests that there may be a relationship between coal chlorine content and mercury oxidation across SCR catalysts and that the Rockport data are consistent with observed full-scale data. The scatter in the data may relate to the effect of catalyst type, ash, other flue gas constituents or the sulfur content of the coal.

In Figure 13, the full-scale mercury oxidation is displayed as a function of coal sulfur content. (For three of the units, the coal sulfur content was estimated from the SO_2 in the flue gas or from the coal origin.) There does not appear to be a strong relationship between mercury oxidation and coal sulfur content. Laboratory experiments have not demonstrated a strong effect of SO_2 on mercury oxidation across SCR catalysts, nor do the full-scale data show a clear effect of SO_2.

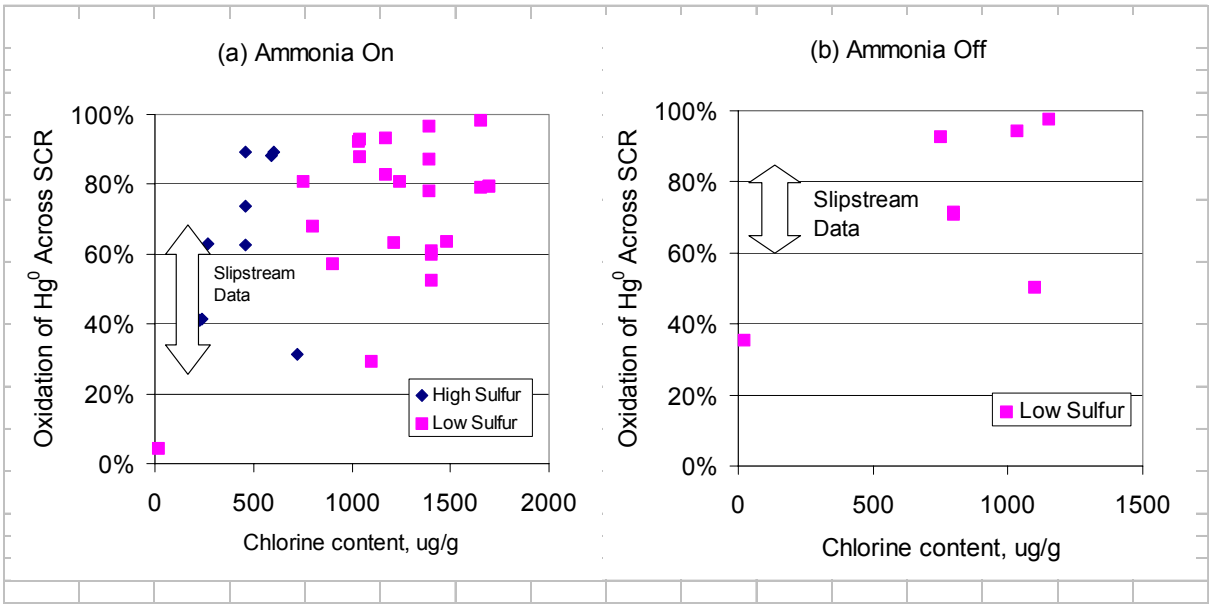


Figure 12. Mercury oxidation as a function of coal chlorine content from full-scale SCR measurements, with and without ammonia; range of values from Rockport slipstream reactor also shown.

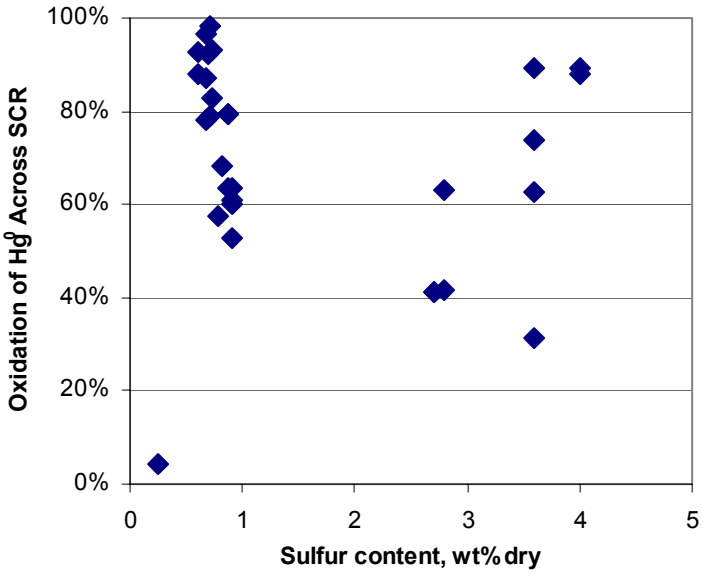


Figure 13. Mercury oxidation as a function of coal sulfur content from full-scale measurements (ammonia on).

Task 5 - Management and Reporting

Results from portions of this research program have been reported to industry through technical presentations at conferences. One paper was presented at the Electric Power Conference, Baltimore, Maryland, March 30-April 1, 2004:

- Constance Senior and Temi Linjewile, "Understanding Oxidation of Mercury Across SCR Catalysts in Power Plants Burning Low Rank Coals."

A paper will be presented next quarter at the Coal Utilization & Fuel Systems Conference in Clearwater, Florida, April 18-22, 2004:

- Constance Senior and Temi Linjewile, "Oxidation Of Mercury Across SCR Catalysts In Coal-Fired Power Plants."

Conclusions

Data were assembled from ten utility boilers at which Hg speciation measurements were made across SCR catalyst and for a number of laboratory and pilo-scale measurements. The data were examined for the relationship between mercury oxidation and parameters such as flue gas composition and space velocity. The slipstream data obtained from Rockport are consistent with both pilot- and full-scale mercury oxidation measurements.

In summary, we can outline a proposed mechanism for mercury behavior in SCR catalysts:

- Hg^0 is adsorbed, possibly on metal oxide sites, where it can be displaced by ammonia and perhaps other constituents of the flue gas.

- Adsorbed Hg^0 reacts with HCl to form $HgCl_2$, though this may not be a direct reaction, but may involve binding of HCl to a surface site or formation of HgO as an intermediate; oxidation increases as temperature decreases.

The type of catalyst affects mercury oxidation, due to both pore structure and composition of the active catalyst sties. The lack of agreement of mercury oxidation data between simulated flue gas and actual flue gas suggests that there are secondary reactions of importance; these might include ash deposits on the catalyst (particularly those high in CaO), SO_3 present in the flue gas and other trace species, particularly radicals.

Plans for Next Quarter

- The preliminary mercury mechanism will be implemented in REI's one-dimensional SCR model.

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