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Investigation of Mercury and Carbon-Based Sorbent Reaction Mechanisms

Mercury Control Technology R&D

Program Review

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Introduction

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of elemental mercury (Hg^0) present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency (EPA) information collection request (ICR) for Hg data showed that Hg^0 ranged from 56% to 96% and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pulverized coal- and cyclone-fired units was dominated by Hg^0 at greater than 85%, and the average amount of Hg^0 emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

In bench-scale sorption tests, the amount of HCl in the flue gas has a significant effect on the initial Hg^0 capture kinetics on carbon-based sorbents, where higher levels (50 ppm HCl) eliminate the induction period. A proposed mechanism for oxidation requires acid activation of the graphene-edge carbene site for oxidation to occur (3). Pretreatment of the sorbent with aqueous HCl has the same effect in bench-scale testing (4), but pilot-scale testing using stored samples of the pretreated sorbent failed to demonstrate an improved sorption capacity.

Goal

- Improve the mercury capture efficiency of carbon-based sorbents through a better understanding of mercury–sorbent reaction mechanisms.

Objectives

- Determine the role of HCl in promoting the oxidation of elemental mercury.
- Determine the role of the carbon structure in providing active sites for oxidation of mercury and SO₂ and the subsequent binding of the oxidation products.
- Evaluate sorbents prepared from coal-based materials provided by project partners.

Scope of Work

Task 1. Flue Gas–Mercury Interactions on the Carbon Sorbent

Task 1.1 – Hydrochlorination Effects on Sorbent Kinetics

Task 1.2 – Evaluation of Surface Chemistry

Task 2. Investigation of the Effects of Surface Modifications on Kinetics and Capture

Task 3. Evaluation of Activated Carbons

Task 3.1 – Evaluation of Activated Carbons

Task 3.2 – Evaluation of Coal Characteristics

Accomplishments

Task 1. Comparison of chlorine impregnation techniques

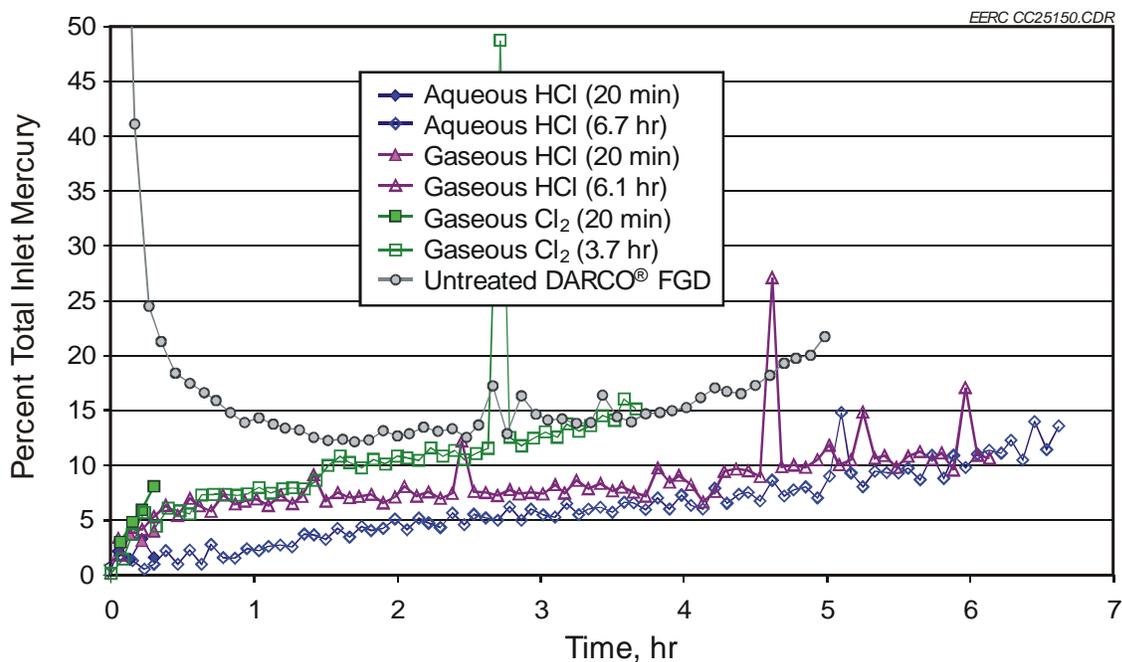
- Bench-scale mercury loading and XPS analysis of DARCO[®] FGD treated with three forms of chlorine at three exposure times
 - Chlorine gas
 - HCl gas
 - Aqueous HCl
- Exposed to low-acid simulated flue gas
 - 6% O₂, 12% CO₂, 15% H₂O, 580 ppm SO₂, 120 ppm NO, 6 ppm NO₂, and 1 ppm HCl
- Three exposure times
 - Starting material
 - After 20 minutes of exposure to low-acid flue gases
 - At 10%–15% breakthrough (3 to 6 hours)

Bench-Scale Loading of Chlorine-Treated FGD Carbons

Test Matrix for Sample Preparation of Pretreated Carbons for XPS Analysis

Test No.	Bench-Scale Exposure Level	DARCO FGD Pretreatment
T1-1 (baseline)	None	HCl(aq)
T1-2	Initial capture (20 min)	HCl(aq)
T1-3	10%–15% Hg breakthrough	HCl(aq)
T1-4 (baseline)	None	HCl(g)
T1-5	Initial capture (20 min)	HCl(g)
T1-6	10%15% Hg breakthrough	HCl(g)
T1-7 (baseline)	None	Cl ₂ (g)
T1-8	Initial capture (20 min)	Cl ₂ (g)
T1-9	10%15% Hg breakthrough	Cl ₂ (g)

Outlet mercury profile during loading of pretreated activated carbons for XPS analysis.



XPS Survey Scan

- The surface became enriched in several mineral elements and oxygen during the aqueous application.
- Sulfur concentrations increased by 5X for the HCl(aq)-treated and nearly 15X for the gaseous-phase treatments.
- Oxygen concentrations increased corresponding to sulfur increase.
- Aqueous application of HCl altered the surface composition of the starting material.
- All three carbons show an increased chlorine concentration ranging from 1.2 to 1.8 at% as compared to <0.1 at% in the untreated carbon.

Surface Characterization of Pretreated Sorbents using XPS Analysis (survey scans normalized to carbon), at%

Test Number	C	O	N	Al	Ca	Cl	Fe	Mg	Na	P	S	Si
Untreated Carbon	86.4	9.3	0.3	0.5	0.9	0.1	0.1	0.1	1.4	0.1	0.1	0.3
T1-1 (baseline)	67	20.9	< 0.1	1.7	1.8	1.4	0.3	4.7	< 0.1	< 0.1	0.8	1.4
T1-2	67.6	22	0.2	1.5	1.2	1	0.2	2.7	< 0.1	< 0.1	2.2	1.4
T1-3	67	29.8	0.22	0.97	1.62	0.65	0.11	0.86	< 0.1	< 0.1	5.19	1.62
T1-4 (baseline)	84.5	9.6	0.4	0.5	1.9	1.2	0.1	0.5	< 0.1	0.2	0.2	0.9
T1-5	84.5	13.2	0.42	0.52	1.04	1.04	0.1	0.62	< 0.1	0.21	1.35	0.94
T1-6	84.5	26.2	< 0.1	0.72	1.8	< 0.1	< 0.1	0.96	0.24	0.12	5.04	0.72
T1-7 (baseline)	85.4	9.3	0.2	0.5	1.4	1.3	0.1	0.6	< 0.1	0.1	0.3	0.8
T1-8	85.4	11.9	0.21	0.51	1.34	1.23	0.1	0.51	< 0.1	< 0.1	0.93	0.82
T1-9	85.4	24.5	0.36	0.48	1.91	0.95	0.12	0.6	< 0.1	< 0.1	4.65	0.6

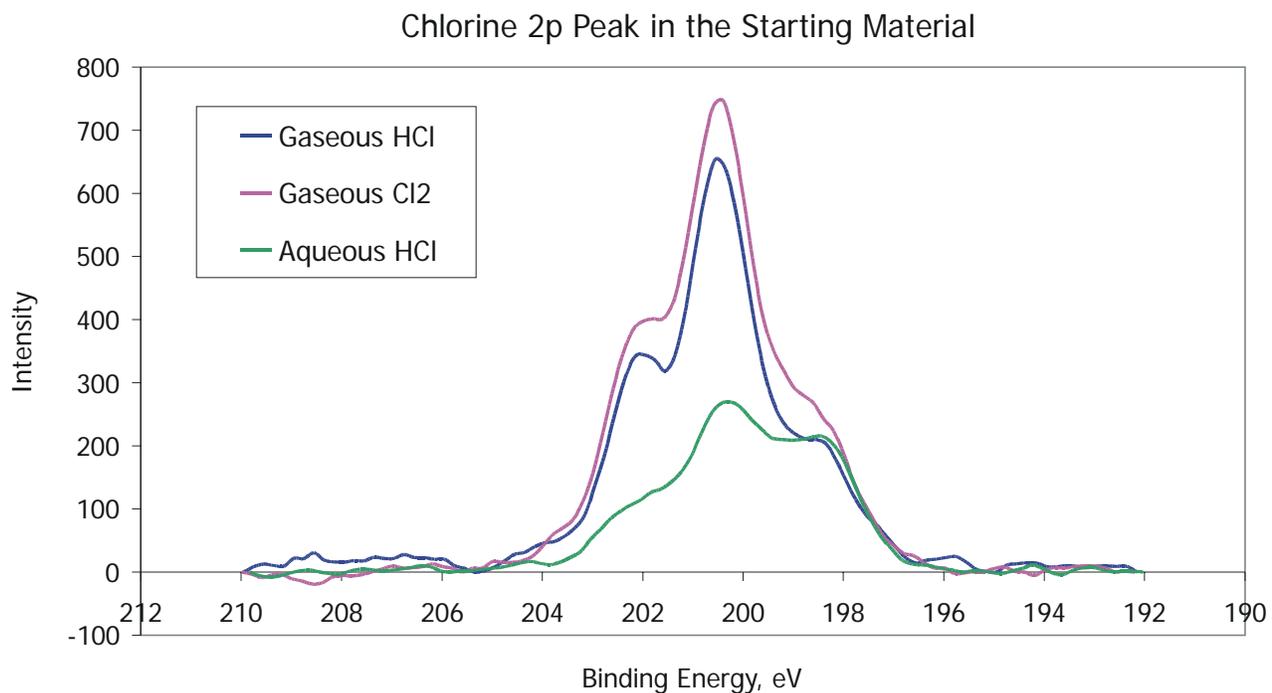
XPS High-Resolution Scans

- Carbon, oxygen, chlorine, and sulfur regions were examined.
- There is insufficient mercury in the samples to overcome the interference of the overlapping silicon peak.
- Understanding the chemical forms of chlorine on the sorbent and the change in its forms with exposure will be beneficial in understanding the mercury–sorbent interactions.

Starting Materials

- The carbon 1s binding region contained one large peak of asymmetric shape typical for carbon black powders or graphitic materials. The peak includes:
 - Single C–C bonding (this may also include some C–H bonding).
 - Broad shake-up structure centered at approximately 291 eV, which is consistent with aromaticity.
 - A low level C–O band of various intensities.
- The oxygen 1s binding region included one large peak.
 - The HCl(*aq*) treatment increased the oxygen concentration.
 - The increase is likely a result of the inorganic constituents leached from the carbon and deposited at the surface.
- The sulfur 2p binding region showed the effects of the chlorine application methods.
 - Gaseous treatments: decrease in sulfide
 - HCl(*aq*) treatment: lost sulfides and gained oxidized sulfur compounds.

Starting Materials

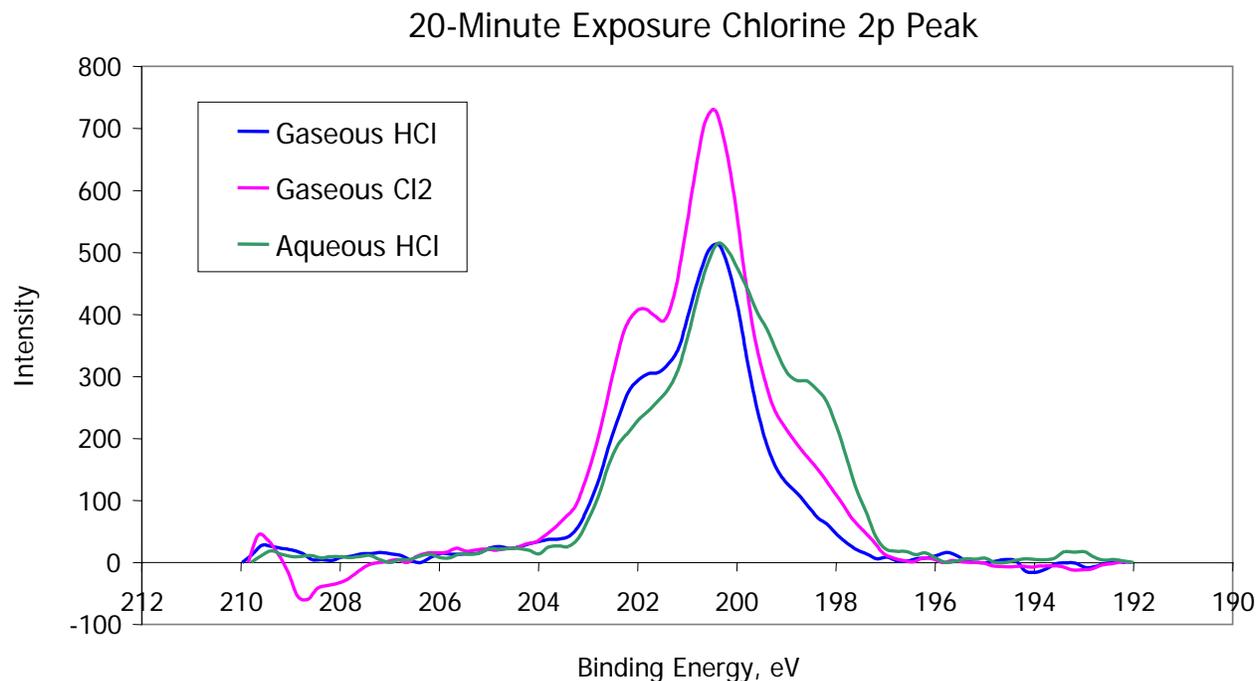


- The chlorine 2p region shows similar chlorine at% content in the three applications (1.2%–1.4%), all of which came from the chlorine addition.
 - Gaseous application: The partitioning of chlorine was 70/30 organochlorine to chloride.
 - *HCl(aq)-treatment*: About half of the chlorine was present as chloride.

20-min Exposure Analysis

- The carbon 1s binding region was similar to the starting materials.
- The oxygen 1s binding region included one large peak.
 - The intensity of all peaks increased, indicating an increased concentration of oxygen (probably as S–O) at the sample surface.
- In the sulfur 2p binding region, the S(VI) peak increased while the thiophene (S[II]) peak diminished, and the sulfide (S[II]) peak disappeared.
 - The buildup of S(VI) on the surface coincides with mercury capture breakthrough and is hypothesized to interfere with the binding of oxidized mercury on the carbon surface.

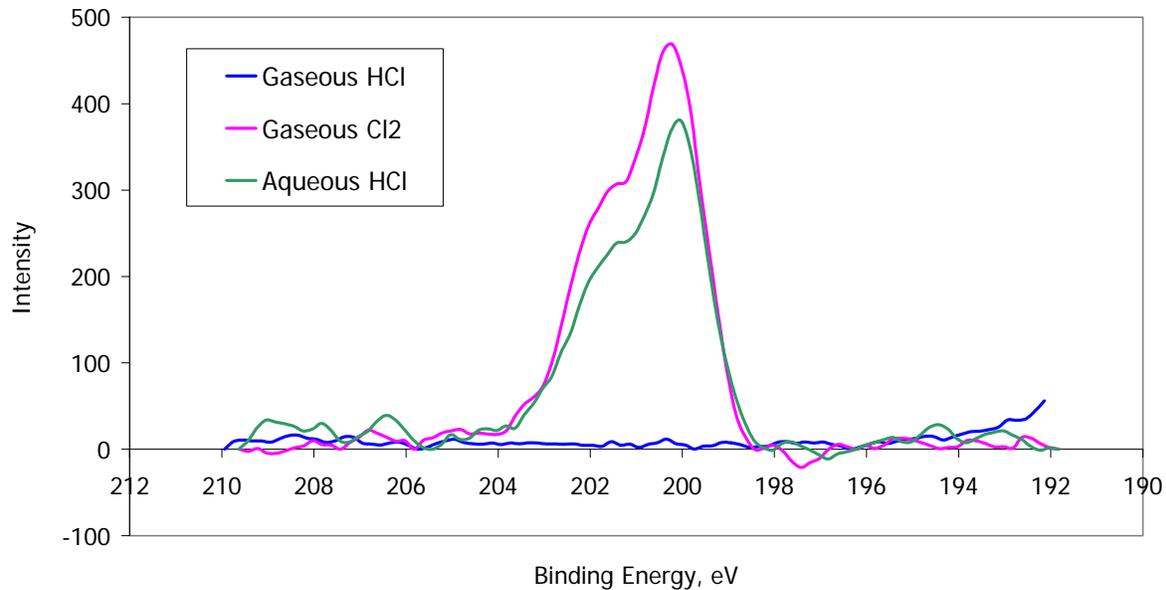
20-min Exposure Analysis



- Cl₂(g) Treated Carbon
 - Loss of Cl⁻.
 - Organochlorine remains nearly constant.
 - Possible loss of occluded Cl₂.
- HCl(g)-Treated Carbon
 - Similar to Cl₂(g)-treated carbon.
- HCl(aq)-Treated Carbon
 - Loss of Cl⁻. More Cl⁻ evolved than for gaseous treatments
 - Organochlorine remains nearly constant.

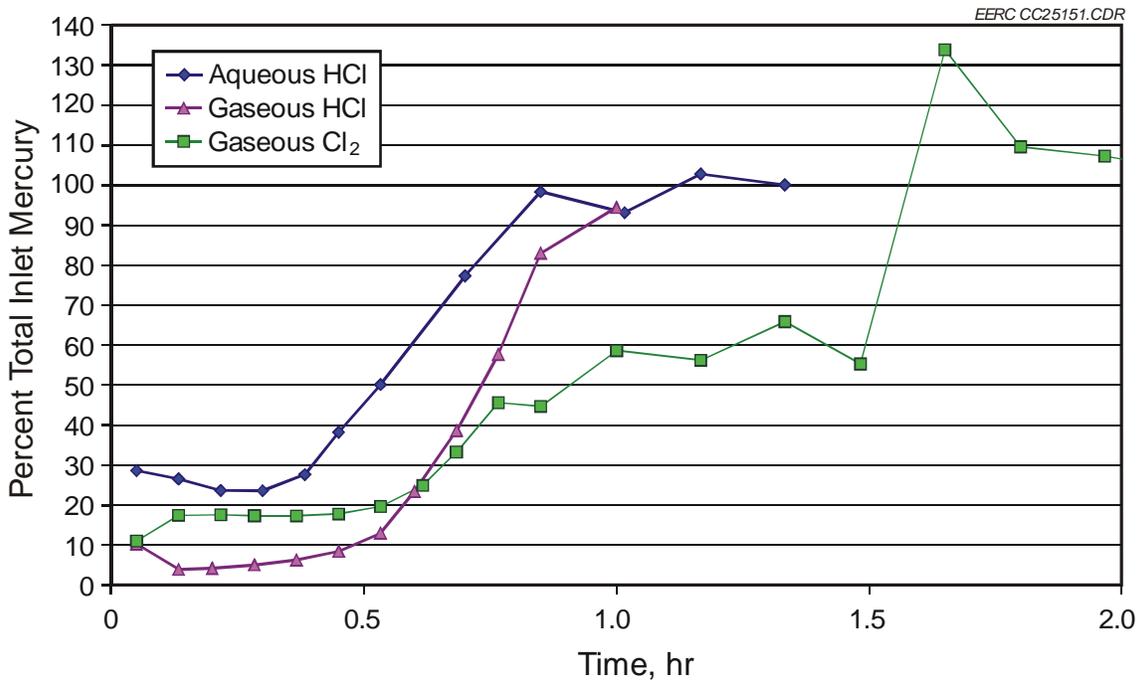
10%–15% Breakthrough Exposure Analysis

10-15% Breakthrough Chlorine 2p Peak



- Cl₂(g) Treated Carbon
 - Loss of HCl.
 - Organochlorine remains nearly constant.
 - Possible loss of occluded Cl₂.
- HCl(g)-Treated Carbon
 - Loss of all Chlorine.
- HCl(aq)-Treated Carbon
 - Loss of HCl.
 - Organochlorine remains nearly constant.

Reactivity Test of the Treated Activated Carbons



- Bench-scale mercury reactivity screening of the three pretreated carbons
 - Chlorine gas
 - HCl gas
 - Aqueous HCl
- Exposed to low-acid simulated flue gas
 - 6% O₂, 12% CO₂, 15% H₂O, 580 ppm SO₂, 120 ppm NO, 6 ppm NO₂, and 1 ppm HCl
 - Until complete breakthrough.
- 37.5 mg carbon diluted with sand (113.5 mg) provide a thin bed.
- Test carried out 5 weeks after the loading experiment was initiated.

Significance

- Inorganic chlorine on the surface is rapidly lost in the flue gas.
- For the Cl_2 - and $\text{HCl}(aq)$ -treated samples, part of the chlorine in the sample is tightly fixed organochlorine and part is more easily displaced.
- For the $\text{HCl}(g)$ -treated carbon, none of the chlorine in the sample is tightly fixed organochlorine.
- Understanding the chemical forms of chlorine on the sorbent and the change in its forms with exposure will be beneficial in understanding the mercury–sorbent interactions.

The Next Step

- Role of sulfur in mercury capture
- Investigation of other techniques for surface analysis
- Evaluation of activated carbons
 - Preparation and mercury activity screening of carbons made from Fort Union lignites
- Evaluation of coal characteristics
 - Coal data analysis to determine availability of desirable coal.

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- Luscar Ltd.
- Westmoreland Coal Company

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