Effect of SCR Catalyst on Mercury Speciation

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Background

- Speciation influences emissions control
 - Wet FGD captures high percentage of ionic Hg²⁺
 - Volatile elemental Hg⁰ is difficult to capture
- Many Selective Catalytic Reduction (SCR) units are meeting stringent NO_X regulations
 - 100 GW coal-fired capacity will employ SCR by 2005
 - Oxides of vanadium/titanium (V₂O₅/TiO₂) catalyst
 - Ammonia (NH₃) or urea (NH₂CONH₂) reductant
- SCR has an impact on mercury speciation
 - Limited field data in Europe and U.S.
 - Increase in Hg²⁺ across SCR reactor

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Hg Chemistry in SCR Systems

- Apparent dependence on coal type
 - Higher Hg²⁺ across SCR for bituminous coal-fired boilers
 - Little change in Hg speciation across SCR for subbituminous (Powder River Basin, [PRB]) coal-fired boilers
- Possible effects of SCR system
 - Changes in flue gas chemistry (NO_X, NH₃, SO₃)
 - Catalytic oxidation by vanadium based catalysts
- Effects of SCR catalyst age and residence time on Hg⁰ oxidation are not well understood
 - Important for SCR to be a viable technology for Hg speciation modification

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- Evaluate Hg speciation effects of SCR technology for Illinois bituminous and PRB coal combustion flue gases
 - No prior SCR Hg field studies on Illinois coals
- Understand the effects of SCR catalyst age and residence time on Hg⁰ oxidation



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Approach

- Pilot-scale SCR experiments
 - Assess Hg⁰ oxidation during firing of Illinois and PRB coals with Ontario Hydro (OH) method
- Bench-scale SCR experiments
 - Fresh and aged catalyst from bituminous coal-fired utility power plant
 - Field-aged sample collected after 2 ozone seasons
 - Residence time studied by varying catalyst length (at constant flow)
 - Simulated flue gas and SCR operating conditions
 - Triplicate run with on-line Hg⁰ analyzer (Seefelder)



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Pilot-Scale Coal Combustion and SCR System



- Vertical down-fired combustor (6"ID X 13'L)
- 150 kBtu/hr firing rate
- Two SCR catalysts (1.25 m each)
- 2 Sootblowers
- SV: ~ 3000 hr⁻¹
- OH sampling at SCR inlet and outlet





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Pilot-Scale SCR Reactor







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Characteristics of Coals Tested

Content	PRB	Turris (Illinois)	Crown II	Galatia (Illinois)
	Black Thunder	(Medium S/Cl)	(Illinois)	(Low S/high Cl)
			(High S/low Cl)	
% Moisture	14.00	16.99	16.07	11.33
% Ash	5.92	9.26	7.34	6.29
% Volatile	37.33	33.89	37.05	34.16
% Fixed C	42.76	39.85	39.55	48.22
HV (Btu/lb)	9,903	10,531	10,877	12,179
%C	59.71	59.00	60.48	68.31
%H	3.83	4.32	4.70	4.50
%N	0.82	1.19	1.07	1.50
% S	0.29	3.11	3.48	1.13
%O	15.44	5.96	5.73	6.94
%Cl	NA	0.17	0.13	0.29
Hg, ppmw	NA	0.07	0.07	0.09

NA: not available

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Pilot-Scale SCR Test Conditions

Parameter	Turris	Galatia	Crown	PRB
			Π	
Coal feed rate, lb/hr	14.0	11.5	13.4	15.7
Firing rate, Btu/hr	147,540	140,424	145,208	155,873
Total air flow, scfm	28.6	28.2	28.4	28.9
Excess air, %	11	18	11	5
CO, ppm (dry)	38	30	40	0
Uncontrolled NO _x ,	960	850	650	525
ppm (dry)				
SO_2 , ppm (dry)	2921	929	2739	222
Air in-leakage	4	4	11	16
(calculated), %				

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Pilot-Scale SCR Test Conditions (Continued)

Parameter	Turris	Galatia	Crown	PRB
			11	
Temperature, °C	365	342	352	364
NOx reduction across				
SCR, %	90	86	90	90
HCl (measured), ppm		216		
(wet)	INIM	246	INIM	INIM
HCl (calculated), ppm	1/1	208	06	7.0
(wet)	141	208	90	7.9
PM at SCR inlet*,	5962	2070	2046	7/10
mg/dscm	3803	3070	3940	2418
PM at SCR outlet*,	2506	1725	2560	1606
mg/dscm	3300	1/33	2300	1000

NM: Not Measured

* Measured using the filter weight of the isokinetic OH method at the inlet and outlet of the SCR

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Illinois Bituminous Coal Test Results

SCR Inlet SCR Outlet



Mercury Speciation

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Black Thunder (PRB) Test Results

SCR Inlet SCR outlet





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Summary of Pilot Results

	Turris	Galatia	Crown	PRB	PRB
			II		Repeat
% Hg ⁰ at SCR inlet	68	73	84	97	96
% Hg ⁰ at SCR outlet	9	4	12	88	76
% Oxidation	87	94	85	9	21



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Bench-Scale SCR Reactor



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Bench-Scale SCR Reactor



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Experimental Procedures

- Thermal pre-treatment of catalyst
 - Heating of catalyst overnight at 425 °C under N₂ flow
 - Minimize residual effect from previous experiment
- Catalyst pre-conditioning
 - Passing SO₂ and HCI through catalyst overnight at levels for next day's experiment
- Add Remaining flue gas components (O₂, CO₂, H₂O, NO, NH₃, Hg⁰) before experiment

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Simulated Bituminous Bench-Scale Results

	Design SV		High SV	
	Fresh	Aged	Fresh	Aged
Space Velocity (hr ⁻¹)	2263	2263	3031	3031
NO _x Reduction (%)	84	90	92	90
	87	86	91	92
	87	85	91	92
Average Reduction (%)	85 <u>+</u> 2	87 <u>+</u> 3	91 <u>+</u> 1	91 <u>+</u> 1
Hg ⁰ Oxidation (%)	87	84	74	70
	88	86	78	68
	89	85	77	68
Average Oxidation (%)	88 <u>+</u> 1	85 <u>+</u> 1	76 <u>+</u> 2	69 <u>+</u> 1

- Aged catalyst sample: collected in the field after 2 ozone seasons (ca. 8000 hr)
- Operating conditions: 365 °C, 2250 ppm SO₂, 590 ppm NO_x, 531 ppm NH₃, 40 ppm HCl, 20 ppb Hg⁰, 4.2% O₂, 13.2% CO₂, 7.1% H₂O



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- Heterogeneous reactions over SCR catalyst promote Hg⁰ oxidation
- Pilot studies confirm coal type dependence
 - Illinois bituminous coal high levels of Hg⁰ oxidation
 - PRB coal low Hg⁰ oxidation at test conditions
- Bench-scale studies show sustained Hg⁰ oxidation
 - Field-aged and fresh SCR samples high Hg⁰ oxidation
 - Slight aging effect seen at high space velocity
- Implications
 - Illinois/bituminous SCR + FGD is a practical option
 - PRB/sub-bituminous SCR oxidation needs improvement

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