Getting Mercury Out of Coal Combustion Gases

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EPA Region 5 Science Forum – October 6, 2004 – Chicago, IL

Outline

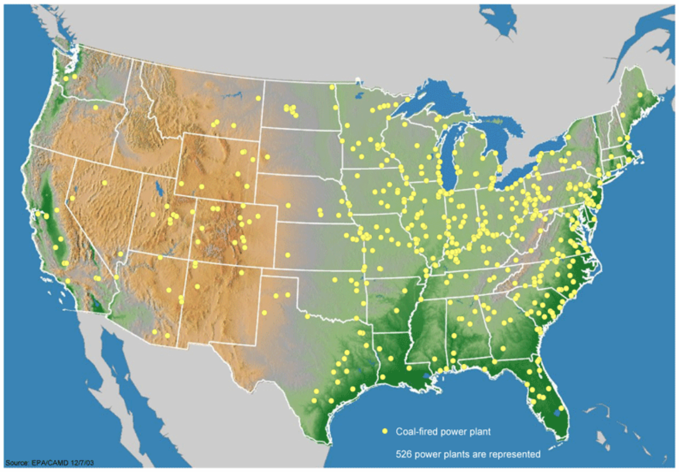
- Background
  - Mercury (Hg) sources and health impacts
  - Regulatory alternatives
- Mercury in power plants
- Mercury control technologies
- EPA's mercury research program

Background

- Hg known to bioaccumulate in human and animal tissue in its most toxic form: methyl mercury
- Human exposure associated with serious neurological and developmental effects
- EPA regulated municipal waste combustors (MWCs) and medical waste incinerators in 1990s; controlled more than 40 tons
- Coal-fired power plants now major source; 48 tons (1999)
- On January 30, 2004 EPA proposed regulations for power plant Hg control; March 15, 2004 supplemental proposal; presently in comment under review. Final rule by March 15, 2005

Slide 4

Coal-Fired Power Plants



U.S. Coal-Fired Power Plants

- **There are about 530 power plants with 305 gigawatt of capacity that consist of about 1,300 units, 1,150 of which are >25 megawatt.**
- **Coal plants generate the vast majority of power sector emissions:**
  - **100% of Hg**
  - **95% of SO_2**
  - **90% of NO_X**

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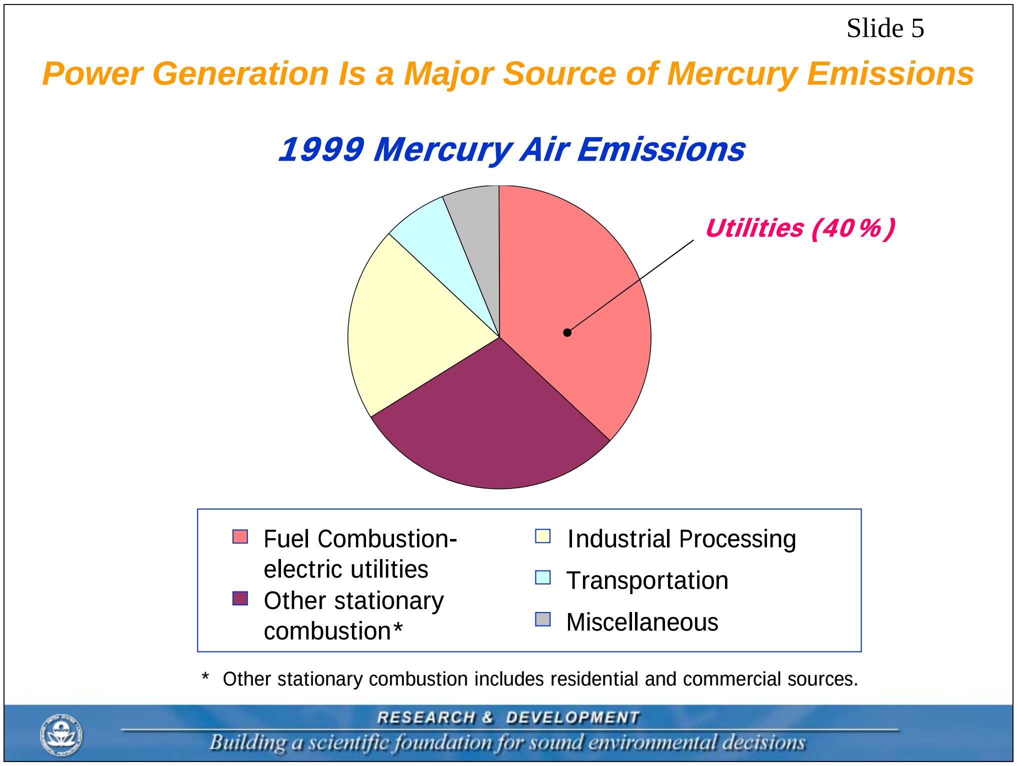
Coal-fired plants are scattered throughout the U.S.

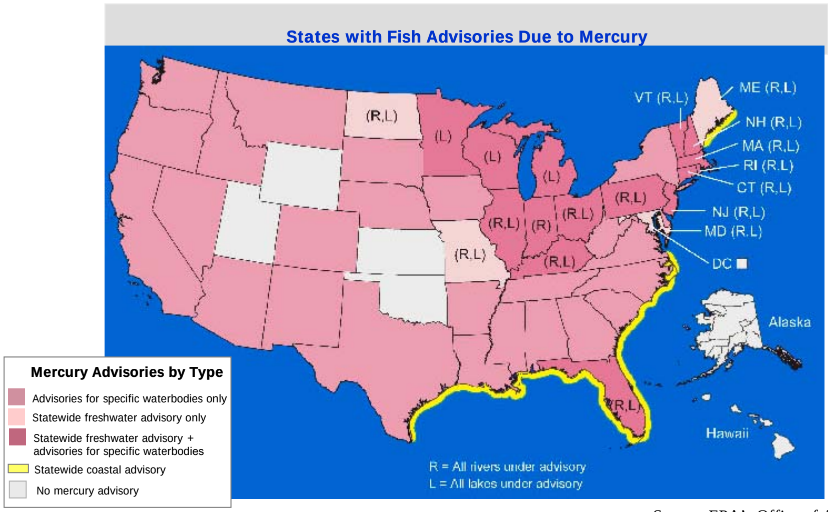


Utilities are major emitters of several pollutants of concern

Slide 6

Mercury Contamination in Fish

- **Currently 44 states have issued fish consumption advisories for some or all of their waters due to contamination from mercury.***



*For more information about the relationship between fish advisories and human exposure to mercury, see the EPA Report "America's Children and the Environment: Measures of Contaminants, Body Burdens, and Illnesses" available at *http://yosemite.epa.gov/ochp/ochpweb.nsf/content/publications.htm*

Source: EPA's Office of Air and Radiation

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Widespread influence of mercury emissions.

Proposed Regulatory Alternatives

- **3 approaches outlined in the January 30, 2004 proposal**
  - Propose traditional, command-and-control section 112 MACT requirements for utility units
    - Reduces mercury emissions from 48 to 34 tons by January 2008
  - Propose cap-and-trade approach under guidelines outlined in section 112(n)(1)(A)
  - Propose market-based, cap-and trade approach under section 111
    - Revises December 20, 2000 finding that it is "appropriate and necessary" to regulate Utility Units under section 112
    - Caps mercury emissions at 15 tons in 2018; interim cap for 2010 proposed to encourage early reductions in SO_2 and NO_X, generating additional Hg emissions reductions

- **Final approach to be determined following completion of public hearings and close of public comment period**
  - Final rule signed on/before March 15, 2005

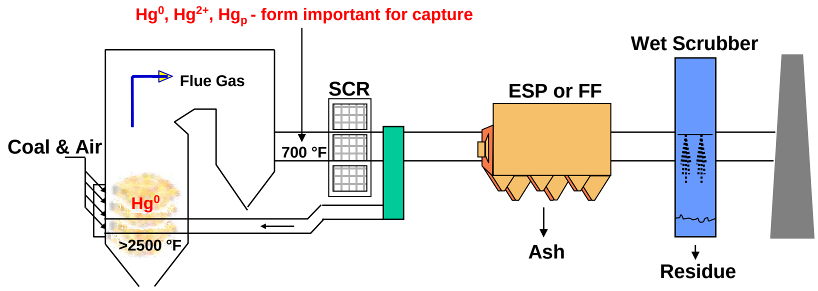
To Learn More…

Utility Mercury Reductions Rule

- **Website:** http://www.epa.gov/mercury
- **Docket no.** OAR-2002-0056
  (Electronic docket: http://www.epa.gov/edocket)

Slide 9

Power Plant Equipment and Mercury



<u>Removal in PM Controls</u>
Mercury adsorbed in fly ash/sorbent, which is captured in ESP or FF; Hg^{2+} compounds are more readily adsorbed than Hg^0

<u>Capture in Wet Scrubbers</u>
Hg^{2+} compounds absorbed in scrubbing solution; Hg^0 is insoluble and cannot be captured; capture enhanced by SCR

Slide 10

Factors That Influence Mercury Control from Coal-Fired Boilers

- Coal type
- Time/temperature profile
- Flue gas composition (chlorine) and fly ash characteristics (carbon, calcium, iron, porosity)
- Air pollution controls already in place

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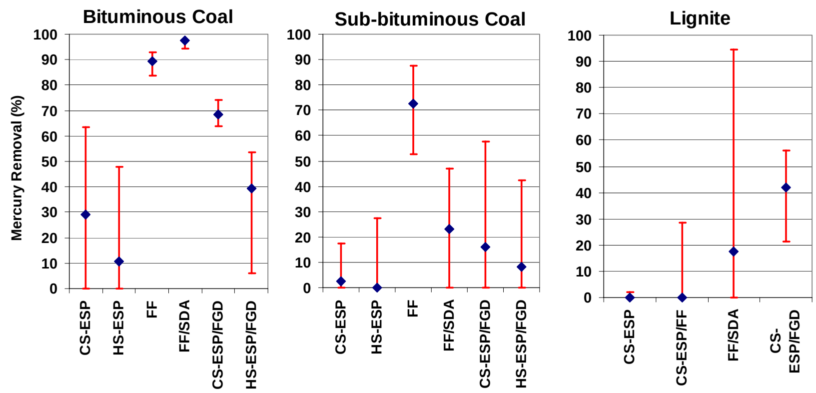
ICR Data – Capture in Existing Equipment



- **Higher levels of Hg capture for bituminous coal-fired plants compared to low-rank coal-fired plants**
- **Large ranges of Hg capture observed**
- **Compared to electrostatic precipitators (ESPs), fabric filters (FF) capture higher levels of Hg**
- **Limited data suggested that scrubbers could potentially capture oxidized Hg effectively**

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C-ESP vs. H-ESP: T effect; Hg^0 not so well.

FF: much better than C-ESP; good for both Hg^{2+} and Hg^0.

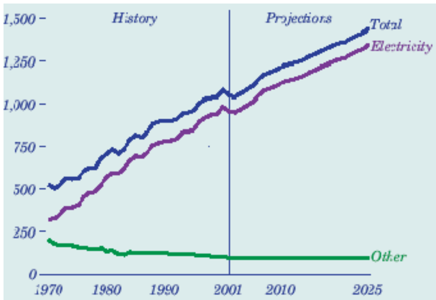
SDA + FF vs. FF: improved capture of Hg^{2+}, but worse capture of Hg^0; acidic Hg^{2+} compounds captured on lime and flyash, but neutral Hg^0 is captured on flyash only. Moreover alkaline environment due to lime may result in reduced number of lewis acid sites on flyash. This, in turn, may reduce capture of Hg^0 on flyash.

Configurations w/ wet FGD reflect improved Hg^{2+} removal over corresponding configurations w/o wet FGD. Hg0 changes relatively small.

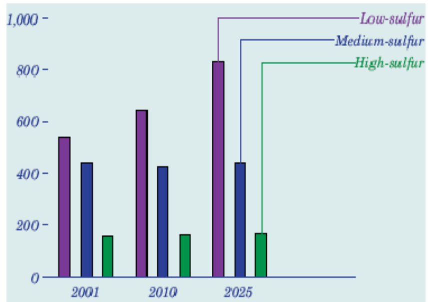
Slide 12

Looking Ahead - Coal Use

Consumption
(million short tons)



Production
(million short tons)



Consumption of low-sulfur coals in the power generation sector is expected to increase in the future.

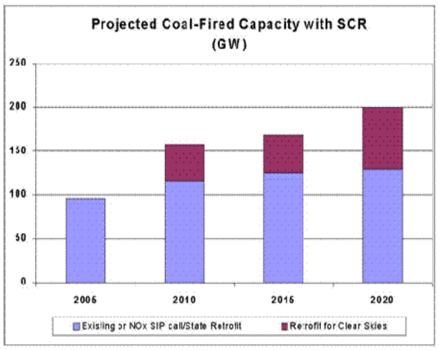
Source: Annual Energy Outlook 2003 with Projections to 2025, DOE/EIA-0383(2003)

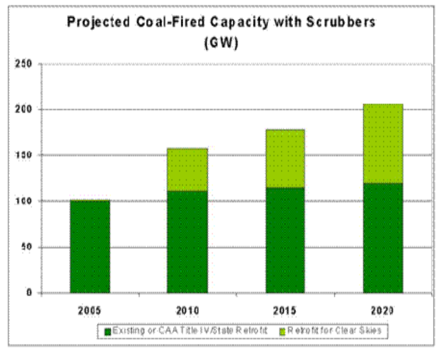
Potential Mercury Control Routes

- Modified (optimized) NO_X, SO_2, and PM controls
- Emerging add-on Hg controls
  - Activated carbon injection
  - Other sorbents
- Sorbent injection + optimized NO_X, SO_2, and PM controls

Slide 14

Looking Ahead – SCR and FGD Projections



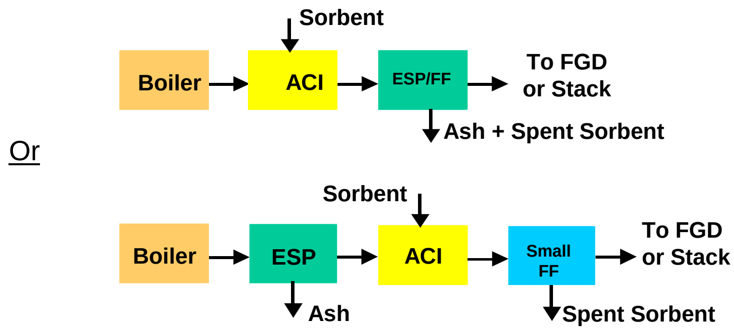


Source: 2003 Technical Support Package for Clear Skies

Slide 15

Sorbent Injection

Two approaches:



The extent of capture depends on:

- **Sorbent characteristics (particle size distribution, porosity, capacity at different gas temperatures)**
- **Residence time in the flue gas**
- **Type of PM control (FF vs. ESP)**
- **Concentrations of SO_3 and other contaminants**

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Activated Carbon Injection (ACI)

ACI system includes a sorbent storage silo and a sorbent injection system. It may also include an added fabric filter to capture the carbon.

Activated carbon injection system

Activated carbon storage and feed system

Source: ADA-ES

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Initial Short-Term, Full-Scale, ACI Projects

Test Site Information			Mercury Capture, %		
Test Site	**Coal**	**Particulate Control**	**Baseline**	**ACI Test Results**	**Test Duration**
PG&E Brayton Point, Unit 1	Low-sulfur bituminous, Hg = 0.03 ppm, Cl = 2000-4000 ppm	Two ESPs in series	90.8	94.5	ACI for two 5-day periods; 10 lb/mmacf
PG&E Salem Harbor, Unit 1	Low-sulfur bituminous, Hg = 0.03-0.08 ppm, Cl = 206 ppm	ESP	90.8	90	ACI for one 4-day period; 10 lb/mmacf
Wisconsin Electric Pleasant Prairie, Unit 2	Subbituminous, Hg = 0.11 ppm, Cl = 8 ppm	ESP	5.3	66	ACI for one 5-day period; 11.3 lb/mmacf
Alabama Power Gaston, Unit 3	Low-sulfur bituminous, Hg = 0.14 ppm, Cl =169 ppm	ESP + small FF	0	90.6 (78)	ACI for one 9-day period; 1.5 lb/mmacf

Note: Short-term tests, variability in Hg emissions, impacts on plant operation, unique test conditions, limited capture of Hg for low-rank coal, amount of carbon injected affects the level of capture.

Slide 18

Brominated B-PAC Carbon Sorbent

- EPA SBIR Phase I and Phase II
  - Manufacture of New Low-Cost High-Temperature Mercury Sorbent for Duct Injection at Electric Utilities
- Sorbent Technologies Corporation
  Twinsburg, OH
  Sid Nelson Jr, President
  Snelsonjr@SorbentTechnologies.com
  (330) 425-2354

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B-PAC Appears Broadly Applicable

Coal	PM Unit	Hg Removal	@lb/MMacf	@ Plant	Scale	Data
Bitum. Low-S	FF	94%	0.5	Valley	Slipstream	Apogee
Bitum. High-S	CS-ESP	70%	4.0	Lausche	Full-Scale	SorbTech
Bitum. Low-S	HS ESP	>80%*	6.4	Cliffside	Full-Scale	SorbTech
Subbitum.Blend	CS-ESP	90%***	3.0	St. Clair	Full-Scale	SorbTech
Subbituminous	CS-ESP	90+%	3.0	St. Clair	Full-Scale	SorbTech
Subbituminous	CS-ESP	89%	4.9	Pleasant Prairie	Slipstream	Apogee
Subbituminous	FF	87%	0.5	Pleasant Prairie	Slipstream	Apogee
Subbituminous	SD/FF	82%**	<1.8	Holcomb	Slipstream	ADA-ES
Lignite	SD/FF	95%	1.5	Stanton 10	Full-Scale	EERC
Lignite	CS-ESP+	70%+	1.5	Stanton 10	Full-Scale	EERC

* when under low-load conditions. STC will return in the fall for improved runs.
** on-fabric removal only, with no in-flight opportunity and the effective "injection rate" could have been significantly lower.
*** data from only the first two weeks of parametric testing; more extensive data to come.
\+ actually the in-flight Hg removal across the spray dryer, with an injection rate of only 1.5 lb/MMacf.

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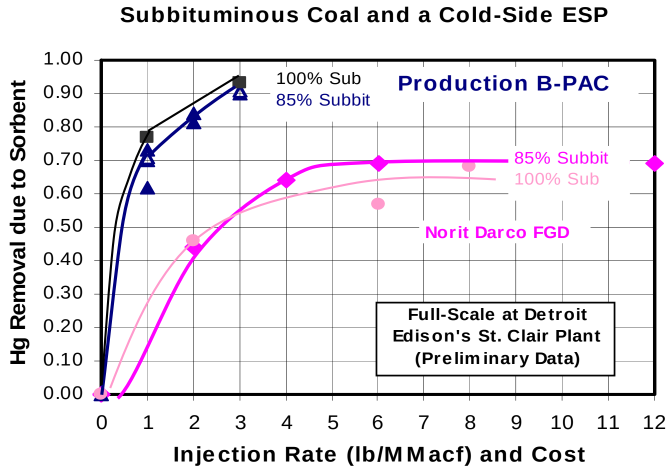
Slide 20

Initial B-PAC Injection Tests at St. Clair Power Plant



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Relative Capital Costs

	$/kW
SO_2 Scrubbers	**$200**
NOx SCR	**$120**
Toxecon™Baghouse	**$60**
PAC Injection alone	**<$2**

With PAC Injection alone:

- Almost no installation time needed
- Little trade labor needed
- Costs are incurred only when operating
- No losses if scrubbers installed later

Slide 22

B-PAC is Now Commercially-Available

- World's first dedicated mercury sorbent production plant
- Can permanently serve a number of power plants
- Estimated price of $1.00/lb today, $0.75/lb with E-o-S
- B-PAC^{TM} is now available in quantity for utility trials & permanent commercial use
- 6+ more plant trials in works

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Amended Silicate Sorbents

- EPA SBIR Phase I and Phase II
  - Development of New Silicate Sorbents to Capture and Immobilize Vapor-Phase Mercury and Mercury Compounds
- ADA Technologies, Inc.
  Littleton, CO
  Jim Butz, Project Director
  www.adatech.com
  (800) 232-0296

Slide 24

Amended Silicates™

- Amended Silicates™ are inexpensive, non-carbon substrates amended with mercury binding sites
- Silicate-based substrate, chemically similar to the native fly ash - no impact on sale of fly ash
- Sites react with elemental and oxidized mercury species to bind the mercury to the sorbent
- Patented
- Generation 1 materials have been tested at full scale
- Generation 2 materials with higher capacity and lower cost to be tested at a power plant in October 2004

Slide 25

Attributes of Amended Silicates™

- **High mercury-capture capacity** – equal or exceeding that of activated carbon.
- **Low cost** – provides a cost-competitive alternative to other sorbent materials (e.g., activated carbon)
- **Little impact to ongoing operation** – uses readily available and demonstrated injection equipment
- **Reliable mercury control** – performance not affected by low chlorine coals, moisture, or acid gas constituents
- **Maintains commercial viability of fly ash as a concrete additive** – no effect on fly ash properties for concrete use
- **Mercury tightly bound to sorbent** – leaching tests via TCLP indicate "below-detection" for mercury.

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Slide 26

Other Mercury Sorbents

- Other halogenated PACs (e.g., Norit's E-3
- Sodium Tetrasulfide
  - Commercially used in Europe on waste incinerators
  - Avoids ash disposal issues
- Mercury Control Absorption Process (MerCAP)
  - Sorbent-coated (gold) metal plates suspended in flue gas
  - Slipstream tests at Great River Power, WEPCO, and Minnesota Power plants
- Sorbents from Waste Tires (AFR)

Sources: Babcock Power, 2003 Mega Symposium, DOE releases

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Anthony Licata
Roderick Beittel
Terence Ake

COAL-FIRED POWER PLANT MERCURY CONTROL BY INJECTING SODIUM TETRASULFIDE
ICAC FORUM 03'
NASHVILLE, TN, OCT 14-15, 2003

http://www.netl.doe.gov/publications/factsheets/program/Prog054.pdf

Slide 27

Low-Cost Mercury Sorbents Derived from Waste Tires
Advanced Fuel Research, Inc. – EPA SBIR Contract No. 68-D-03-039

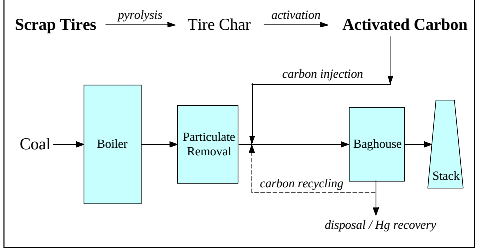
Objectives: (1) removal and recovery of mercury from combustion/incineration flue gas; (2) reprocessing of waste tires into value-added products.

Approach: mercury adsorption on low-cost, sulfur-rich activated carbons derived from scrap tires. The sulfur added to tire rubber during vulcanization makes tire-derived sorbents particularly effective in mercury control due to the high chemical affinity between mercury and sulfur.

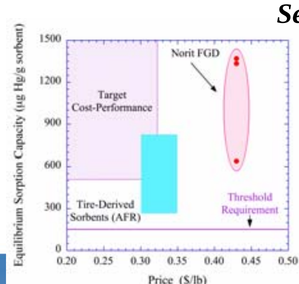
Applications: coal-fired power plants; municipal, medical, and hazardous waste incinerators.

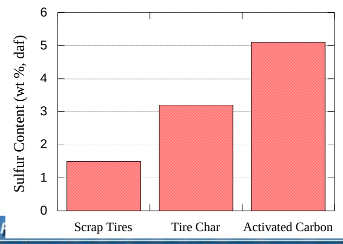
Implementations: (1) sorbent injection into the flue-gas duct (near-term applications); and (2) a patented regenerative scheme (long-term applications) - U.S. Patents No. 6,103,205 and 6,322,613.

From Solid Waste to Mercury Sorbents



Selected Results





Contact Information:
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Web: www.AFRinc.com

AFR

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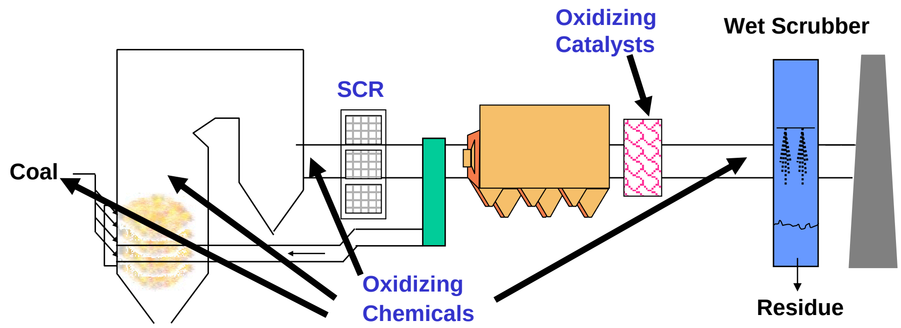
Slide 28

Enhancing Hg Removal in Wet Scrubbers

Increase the amount of Hg^{2+} in flue gas

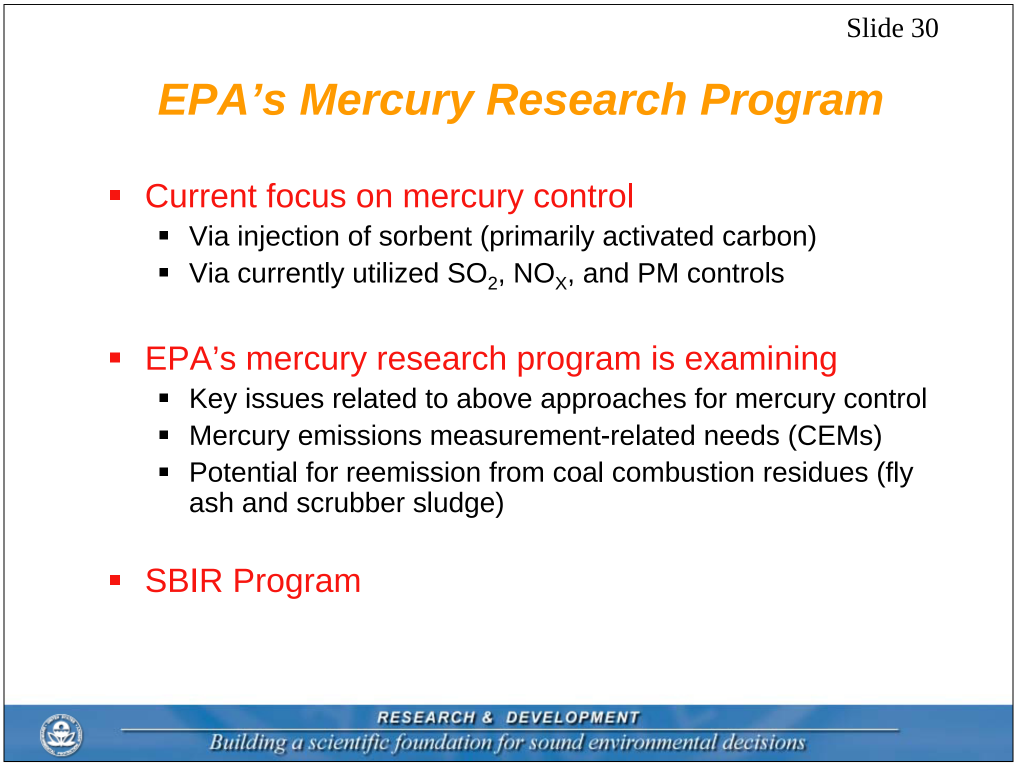


SCR – Ongoing full-scale measurements: ~85- 90+% Hg removal for SCR + PM control + wet scrubber with bituminous coals; performance with low-rank coals uncertain. Effects of catalyst volume and aging need investigation. Optimize SCR for Hg capture.

Oxidizing catalysts and chemicals – under development

Summary & Conclusions

- Hg capture with existing controls depends on coal and technology type; more difficult to control Hg from low-rank coal-fired boilers.
- Sorbent injection (including ACI) is an emerging Hg control technology.
- Hg control of 90% using ACI with a fabric filter for all coals is potentially achievable by 2007.
- Sorbents other than ACI are under development via EPA's Small Business Innovative Research program and by others.



EPA has taken regulatory actions to control emissions of Hg from coal-fired utility plants. The final Hg rule is scheduled to be issued in December of this year (2004).

There is an urgent need to make available cost-effective control technologies in the 2010-2015 timeframe.

Effective mercury control is very coal-type dependent and on the type(s) of air pollution control that are already in place. There are many opportunities for co-benefit Hg control with existing technologies for control of SOx (wet scrubbers), NOx (selective catalytic reduction, SCR) and particulate matter (PM) control. Many of our current programs are currently exploring those opportunities.

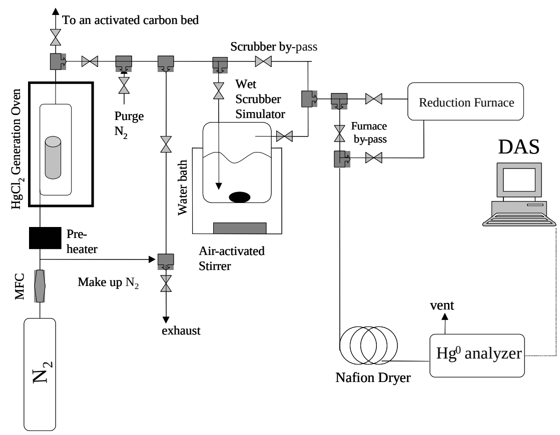
We are continuing to collaborate with DOE, EPRI, and other organizations in this area.

Mercury Control in SO_2 Scrubbers

Objective: enhance net Hg removal in wet scrubbers by stabilizing dissolved Hg^{2+} to prevent reemission of insoluble Hg^0

Findings:

- Absorbed Hg^{2+} is not stable, a portion of Hg^{2+} can be reduced to Hg^0 and reemitted
- Sulfite/bisulfite and heavy metals can cause reemission
- Additives used for waste water treatment may be able to stabilize Hg^{2+}



EPA Contact: Dr. John Chang, *chang.john@epa.gov*, (919) 541-3747

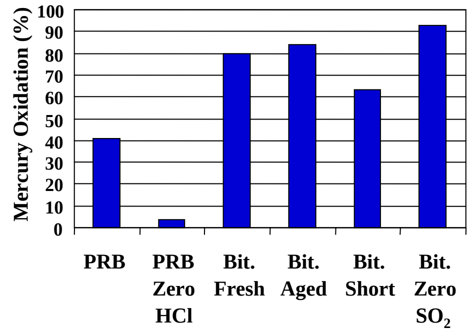
Slide 32

Mercury Oxidation Across SCR Catalyst

Objective: understand the science of Hg^0 oxidation across SCR catalysts, and develop approaches to control the extent of this oxidation

Findings:

- HCl is a key source of chlorine needed for Hg^0 oxidation
- No apparent effect of catalyst aging
- Effect of residence time on oxidation
- No apparent effect of SO_2 on oxidation



EPA Contact: Dr. C.W. Lee, *lee.chun-wai@epa.gov*, (919) 541-7663

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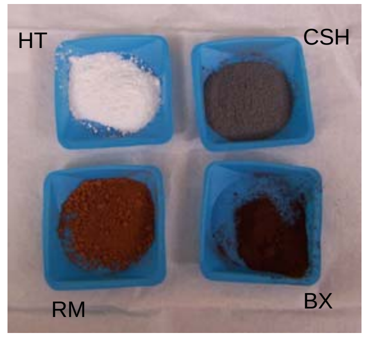
Results are consistent between the in-house pilot tests and field tests

Development of Multipollutant Sorbents

Objectives:
- Synthesis, Characterization, Evaluation & Optimization
- Relate structure and chemical nature to adsorption characteristics



Adsorption capacity at 80 ˚C, 1-hr

Sorbent	SO_2 (mg/g)	NO_X (mg/g)	Hg (ug/g)
Activated Carbon	35.9	0.5	**58.0**
$Ca(OH)_2$	64.8	3.2	0.5
EPA-1 (CSH)	**130.5**	10.6	30.9
EPA-2 (HT)	122.8	**16.4**	4.8
EPA-3 (RM)	20.9	0.3	50.1
EPA-4 (BX)	33.0	0.8	41.3

EPA Contact: Dr. Nick Hutson, *hutson.nick@epa.gov*, (919) 541-2968

Motivation

Multipollutant sorbents offer an attractive and cost-effective means for removing Hg and other pollutants of interest

Sorbent Development

Synthesis, Characterization, Evaluation & Optimization

Relate structure and chemical nature to adsorption characteristics

Types of Sorbents Being Studied

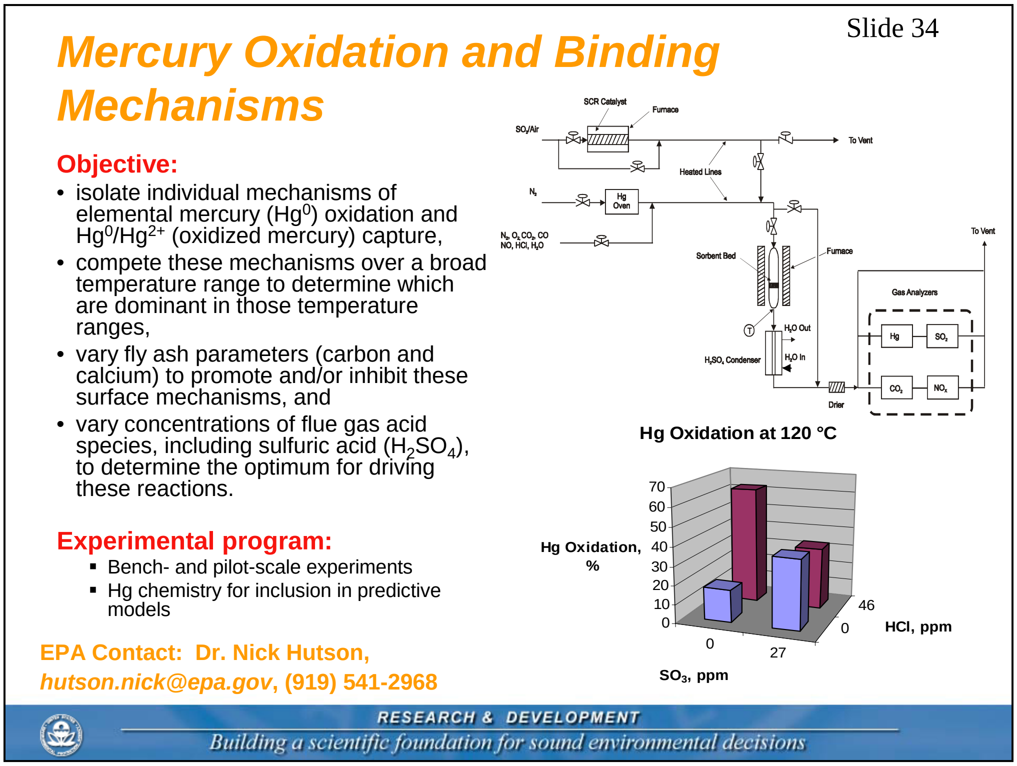
Sorbents synthesized using industrial by-products (fumed waste silica; bauxite residue, *etc.*)

Modified carbonaceous sorbents

Surface modified Calcium Silicate Hydrate (C-S-H)

Hydrotalcite-like compounds (HTlcs) and other layered compounds

Sorbents with catalytic properties



The effective use of fly ash and flue gas cooling/conditioning as a mercury control strategy would greatly reduce the cost of mercury control by potentially reducing or eliminating the need for injection of activated carbon or other external sorbent materials, or, alternatively, reducing the need for scrubber additives, new SCR formulations or adding upstream oxidants for higher FGD mercury removals.

This would also alleviate the potential loss of carbon-contaminated fly ash as a salable byproduct and resultant increased disposal in landfills.

Another benefit is in determining how fly ash and flue gas properties affect sulfuric acid emissions that may lead to concurrent reduction of PM2.5 condensable emissions and mercury by flue gas cooling and conditioning.

Specific configurations are being explored to address issues such as pozzolanic reactions (cementation), turbulence/mass transfer, and corrosion.

EPRI has expressed an interest in working collaboratively in this area.

Multi-Pollutant Control Research Facility (MPCRF)

- State-of-the-art research facility
  - 4 Million Btu/hr (1.2 MW_t) Pulverized-Coal-Fired Facility
  - Evaluate Combinations of Technologies
  - Optimize Control of Multipollutants (SO_2, NO_X, PM, and Hg)
- Incorporates several technology options
  - Electrostatic Fabric Filter (ESFF): Fine PM and Hg Capture
  - Selective Catalytic Reduction (SCR): NO_X and Hg Oxidation
  - Lime Flue Gas Desulfurization (FGD): SO_2 and Hg Capture
  - Conventional and Advanced Sorbents: Hg, SO_2, and/or NO_X
- Future capability
  - Circulating Fluidized Bed: SO_2, Hg, and NO_X
- Collaborative research possibilities

EPA Contact: Dr. Shannon Serre, *serre.shannon@epa.gov*, (919) 541-2968

Slide 36

Hg Control Research on MPCRF

Objective: develop data on activated carbon injection-based mercury capture with ESFF; examine operational concerns, especially impact on bag life

Experimental program:

- Burn different rank coals in the MPCRF
- Characterize removal of Hg by native flyash
- Inject activated carbon prior to baghouse
- Test effect of air-to-cloth ratio, carbon type, carbon feed rate, and gas temperature on Hg removal; examine carbon impact on bag cleaning frequency
- Ontario-Hydro and CEM Hg measurements

EPA Contact: Dr. Shannon Serre, *serre.shannon@epa.gov*, (919) 541-2968

Mercury Measurements

Contributions:

- Major support to OAR and OAQPS
- Demonstration of Hg CEM performance through field testing
- Pilot-plant testing to expedite Hg CEM technology development
- Pilot-plant and field testing of Method 324
- Coauthored proposed regulatory methods PS 12A and 324
- Review, research, revision, and approval of ASTM Ontario Hydro Method
- Development of gaseous standards for Hg CEM operation
- Development of speciated measurement techniques for control technology research

Ongoing activities:

- Continued support to OAR and OAQPS
- Long-term Hg CEM field testing
- Improved QC techniques for proposed Method 324 sampling
- Development of oxidized Hg gas standards
- Improved techniques (e.g., inertial probes) for speciated measurements at PM control inlet locations

EPA Contact: Mr. Jeff Ryan, *ryan.jeff@epa.gov*, (919) 541-1437

Quality Hg measurements (total and speciated) are the key to Hg formation and control research

Slide 38

Evaluation of Potential for Cross-Media Transfers

Objective: investigate the potential for leaching and release of Hg from coal combustion residues

Contributions:

- Development and standardization of analysis protocols
- Evaluation of potential for cross-media transfer
  - Class C and Class F fly ash
  - Scrubber sludge (synthetic gypsum)

Ongoing activities:

- Continued evaluation of fly ashes and scrubber sludge for a spectrum of coal/control technology combinations

EPA Contact: Ms. Susan Thorneloe, thorneloe.susan@*epa.gov*, (919) 541-2968
and Dr. Nick Hutson, hutson.nick@epa.gov, (919) 541-2968

Slide 39

Small Business Innovative Research (SBIR)

- EPA and 11 Federal Agencies
- Priority EPA technology development needs
- Annual solicitations
- Two phases
  - Phase I - $70,000
  - Phase II - $225,000 - $350,000
- Annual budget - $6M

Slide 40

Small Business Innovative Research (SBIR)

- Regular Topics
  - Air pollution control; P2; Water; Waste; Monitoring

- Special Topics
  - Region 1 (2002); Region 8 (2003); Region 9 (2004)
  - Region 3 and Region 10 (2005)
  - Region 5 (2006)

RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions