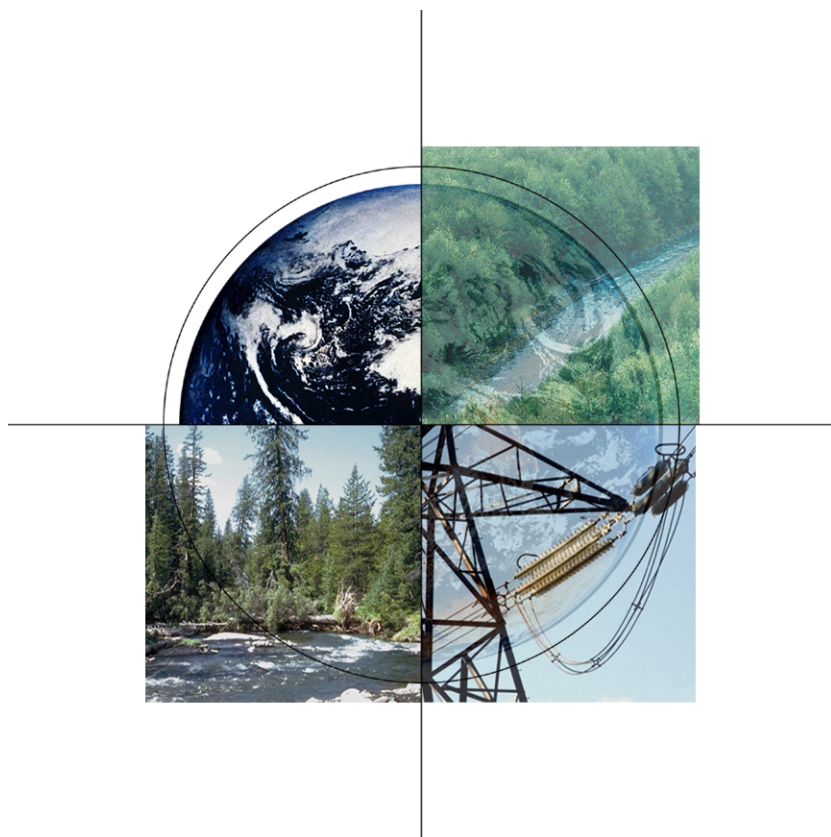


Innovations for Existing Plants Program

DOE/NETL-305/102307



Recent Accomplishments

October 2007



Disclaimer

This report was prepared as an account of work sponsored 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 therein 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 therein do not necessarily state or reflect those of the United States Government or any agency thereof.

The U.S. Department of Energy Innovations for Existing Plants Program

DOE/NETL-305/102307

Recent Accomplishments

October 2007

NETL Contact:

**Thomas Feeley
Technology Manager
Innovations for Existing Plants Program**

Prepared by:

**Dilo Paul
Michael Nemeth
Babatunde Fapohunda
Gregson Vaux
Science Applications International Corporation/
Research Development Solutions, LLC**

**Robb Lenhart
Parsons Corporation/
Research Development Solutions, LLC**

**National Energy Technology Laboratory
www.netl.doe.gov**

TABLE CONTENTS

1.	PROGRAM BACKGROUND.....	1
2.	MERCURY CONTROL TECHNOLOGIES	2
2.1.	Subprogram Summary	2
2.2.	Untreated PAC	3
2.3.	Chemically Treated PACs and Other Sorbents.....	6
2.4.	Tests with High SO ₃ Flue Gas Sites.....	9
2.5.	Full-Scale Field Tests of Technologies Designed to Preserve Fly Ash Recycling.....	10
2.6.	Mercury Co-removal across Wet FGD Systems Using Catalytic Mercury Oxidation.	11
2.7.	Chemical Additives for Elemental Mercury Oxidation	12
2.8.	FGD Additives	12
2.9.	Other Technologies - Multi-Pollutant Control Technologies	13
2.10.	Characterization of Mercury Emissions Via Combustion Modification	13
2.11.	Mercury Control Technologies.....	13
3.	COAL UTILIZATION BY-PRODUCTS.....	16
3.1.	Subprogram Summary	16
3.2.	Development of Advanced Technologies to Expand Market Use for Coal Combustion By-Products.....	16
3.3.	CUB Environmental Research.....	17
3.4.	Industry Collaboratives.....	18
3.5.	NETL Office of R&D	19
4.	WATER-ENERGY INTERFACE.....	19
4.1.	Subprogram Summary	19
4.2.	Non-Traditional Sources of Process and Cooling Water	20
4.3.	Innovative Water Reuse and Recovery.....	21
4.4.	Advanced Cooling Technology	24
4.5.	Advanced Water Treatment and Detection Technology.....	26
4.6.	Systems Analysis and Policy Support.....	28
4.7.	In-House Watershed Science & Technology R&D	29
5.	NO _x CONTROL TECHNOLOGIES	30
5.1.	Subprogram Summary	30
5.2.	Advanced In-Furnace Technologies for Existing and New Plants	31
5.3.	Advanced Post-Combustion NO _x Control Technologies	33
6.	AIR QUALITY R&D	34
6.1.	Subprogram Summary	34
6.2.	Ambient Monitoring	35
6.3.	Emissions Characterization.....	36
6.4.	Predictive Modeling and Evaluation.....	37

1. PROGRAM BACKGROUND

Coal-fired power plants today meet over 50 percent of the U.S. electricity demand. These units, representing a total of nearly 320 gigawatts (GW) capacity, currently generate over 1,900 billion kWh per year. These plants provide cleaner electric power, thanks to novel air pollution control technologies developed over the past few decades. All plants today comply with the regulations of the 1970 Clean Air Act (CAA) and its subsequent amendments in 1977 and 1990 to limit emissions of sulfur dioxide (SO₂), nitrogen oxides (NO_x), and particulate matter (PM₁₀). However, further restrictions on emissions have recently been promulgated in response to issues such as mercury, ground-level ozone, nitrification of aquatic ecosystems, ambient fine particulate matter (PM_{2.5}), and visibility impairment (regional haze). In May 2005, the Environmental Protection Agency (EPA) issued a final regulation for the control of mercury emissions from coal-fired power plants. The Clean Air Mercury Rule (CAMR) establishes a nationwide cap-and-trade program that will be implemented in two phases and applies to both existing and new plants. The first phase of control begins in 2010 with a 38-ton/year mercury emissions cap. The second phase of control requires a 15-ton/year mercury emissions cap beginning in 2018. Meanwhile, several states have adopted or are considering legislation that will impose more stringent regulations on mercury emissions from coal-fired boilers than those included in CAMR. SO₂ and NO_x emissions reductions have also been targeted under EPA's Clean Air Interstate rule (CAIR) that was issued in May 2005. Tighter SO₂ and NO_x emission reductions will be implemented in two phases, with Phase I compliance dates of January 1, 2009 for NO_x and January 1, 2010 for SO₂, and a Phase II compliance date of January 1, 2015 for both NO_x and SO₂. In addition, future regulatory developments may require higher collection efficiencies for PM, particularly for submicron particles, that may not be achievable with electrostatic precipitators (ESP) or baghouses.

Another area for potential regulation is the disposal and/or utilization of solid byproducts, such as fly ash, bottom ash, and flue gas desulfurization (FGD) sludge that are generated from coal-fired power plants. Over 88 million tons of ash (fly and bottom) and 29 million tons of FGD by-products—collectively referred to as coal utilization by-products (CUB)—are produced each year by coal-fired power plants. In addition, these plants withdraw over 132 billion gallons of freshwater each day largely for cooling purposes, competing with freshwater needs for household, industrial, and agricultural use. Further restrictions on cooling water withdrawal under the Clean Water Act and potential tighter drinking water and effluent standards for mercury, arsenic, and other trace metals will place additional constraints on water use in coal-fired power plants.

Such continued tightening of regulations will force the operators of existing coal-fired power plants to retrofit their existing boilers with additional pollutant control technologies, some of which may adversely impact plant efficiency and performance. These expenses come at a time when the industry is faced with rising fuel prices, aging facilities, and an open electric power market that forces bottom-line accounting, resulting in little or no funding for the research and development (R&D) needed to develop the advanced technologies.

To help meet these challenges, the Department of Energy (DOE) Office of Fossil Energy (FE) initiated the Innovations for Existing Plants (IEP) Program, managed by the National Energy

Technology Laboratory (NETL). The IEP program is an integral component of the FE coal and power research portfolio that supports the DOE mission of “protecting national energy and economic security with advanced science and technology and ensuring environmental cleanup” with the strategic goal of promoting a diverse supply of reliable, affordable, and environmentally sound energy. In particular, the IEP program supports the near-zero emissions coal-based electricity and hydrogen production program goal to create partnerships to develop technologies to ensure continued electricity generation and hydrogen production from the extensive U.S. fossil fuel resource base. This effort includes control technologies to permit cost-effective compliance with emerging regulations and ultimately, by 2015, near-zero emission plants that are fuel-flexible, capable of multi-product output, and operate with efficiencies over 60 percent with coal and 75 percent with natural gas. To accomplish this goal, the IEP program involves R&D and technology transfer activities in partnership with industry, government agencies, universities, and national laboratories. The portfolio of activities is divided into six research areas, namely:

- Mercury emissions control
- Coal combustion by-products
- Water management
- Advanced NO_x emissions control
- Air quality research
- Particulate matter and acid gas emissions control

The IEP program portfolio of R&D activities includes laboratory through field-scale demonstration related to the control of mercury, NO_x, PM, and acid gas emissions from coal-based power plants, as well as research in CUB, water use and management, and air quality. Funding on a fiscal year basis has averaged about \$20 million over the past five years.

This document identifies key accomplishments within the IEP program’s portfolio of activities, categorized within the subprograms listed above, except for particulate matter and acid gas emissions control for which there has been no recent R&D activity. Accomplishments are presented by technology and the respective power plants where these technologies were evaluated. Those shown with their titles highlighted in yellow were accomplished in FY 2007.

2. MERCURY CONTROL TECHNOLOGIES

2.1. SUBPROGRAM SUMMARY

The largest subprogram within the IEP Program is the capture and control of mercury from coal-fired power plants. The objectives of this program are to develop:

- An understanding of mercury speciation and capture in coal combustion flue gas
- Reliable measurement techniques for total and speciated mercury

- Cost-effective mercury control technologies for the U.S. fleet of coal-fired power generation facilities

The mercury R&D program has identified several major factors that affect mercury speciation and capture from coal combustion flue gas. Of particular importance is the volatility of mercury and its different forms (i.e., Hg^0 , Hg^{2+}) that pose a challenge for its complete removal. The mercury R&D program developed a mercury removal knowledge base for the development of mercury-specific control technologies for coal-fired power plants. Through a three-phase, full-scale field testing initiative, the IEP Program has brought mercury-specific control technologies to the point of commercial readiness in advance of the regulatory schedules set forth in CAMR and state-level regulations. As of September 2007, about 70 full-scale activated carbon injection systems, a technology developed under the IEP Program, have been procured by U.S. coal-fired power plants. These units produce about 30 GW of electricity, or roughly 10 percent of total U.S. coal-fired power generation capacity. This figure is likely to grow as the regulatory structure for coal-fired mercury emissions becomes clear and utilities develop robust mercury control strategies. The highlights of the mercury R&D subprogram are broadly discussed here within the various categories of mercury control technologies. The first, sorbent injection, is currently the most mature mercury-specific control technology available and an efficient, chemically treated activated carbon injection (ACI) system can reduce total mercury emissions by over 90 percent at a cost that is potentially below \$10,000 per pound of mercury removed (\$/lb Hg removed).

The typical ACI system is located upstream of a particulate control device—either an electrostatic precipitator (ESP) or fabric filter (FF)—to enable simultaneous capture of the spent powdered activated carbon (PAC) and fly ash. This mercury control strategy leads to commingling of the PAC and fly ash that can prohibit certain fly ash recycling avenues. In response, NETL has completed full-scale evaluations of technologies such as the Electric Power Research Institute's (EPRI) toxic emissions control configurations (TOXECON™ and TOXECON II™) as well as non-carbon, concrete-friendly sorbent injection systems designed specifically to preserve fly ash quality.

2.2. UNTREATED PAC

During 2001 to 2002, ADA Environmental Solutions (ADA-ES) conducted untreated PAC injection tests at four power plants: Alabama Power's E.C. Gaston Unit 3, WeEnergies' Pleasant Prairie Unit 2, PG&E's Brayton Point Unit 1, and PG&E's Salem Harbor Unit 1. These tests constituted the Phase I stage of a multi-stage test protocol. Full-scale follow up tests (Phase II) were carried out at Southern Company's Plant Yates Unit 1 and DTE Energy's Monroe Station Unit 4.

Alabama Power's E.C. Gaston Unit 3

The EPRI TOXECON™ configuration, evaluated at the bituminous coal-fired E.C. Gaston Unit 3, achieved over 90 percent total mercury capture across the compact hybrid particulate collector

(COHPAC™)¹ FF with the injection of NORIT Americas's untreated DARCO® Mercury PAC at about 2.5 pounds per million actual cubic feet (lb/MMacf) of flue gas. The TOXECON™ process eliminates fly ash carbon contamination by injecting PAC into an FF located downstream of the primary particulate collection device (Figure 1).

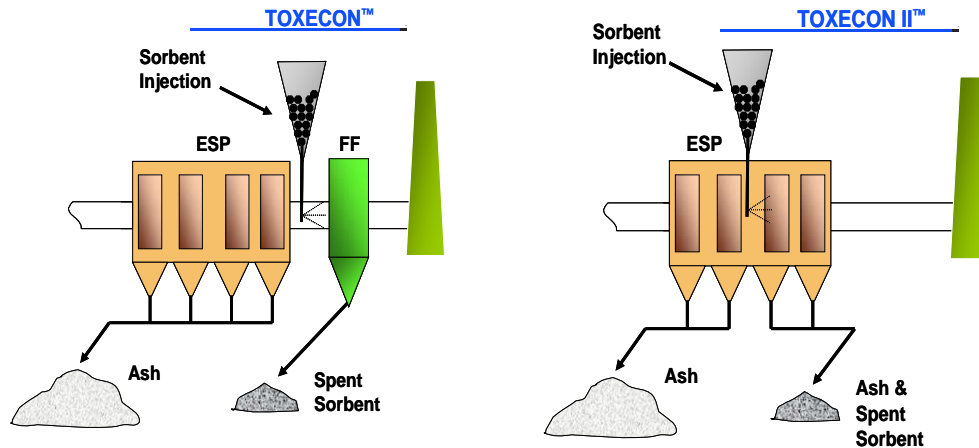


Figure 1. Schematic of TOXECON™ and TOXECON II™ technologies.

WeEnergies' Presque Isle Power Plant

Based on the promising Phase I results at E.C. Gaston, TOXECON™ was selected for a first-of-a-kind commercial mercury control technology demonstration at WeEnergies' Presque Isle Power Plant in Marquette, MI, under the DOE Clean Coal Power Initiative. Currently operational, with an installed capital cost of approximately \$128 per kilowatt (\$/kW) for the retrofit FF, the TOXECON™ configuration has achieved about 90 percent total mercury removal with untreated DARCO® Hg and brominated DARCO® Hg-LH injection at about 3 and 2 lb/MMacf, respectively. During an extended testing period, greater than 90 percent total mercury removal was maintained for 48 consecutive days with both DARCO® Hg and DARCO® Hg-LH injection.

WeEnergies' Pleasant Prairie Unit 2

Field testing of the DARCO® Hg injection, conducted upstream of a cold-side ESP (CS-ESP) at this Powder River Basin (PRB) subbituminous coal-fired unit, showed total mercury removal was limited to about 65 percent despite ACI concentrations as high as 30 lb/MMacf. This may have been caused by the low hydrogen chloride (HCl) concentrations in the flue gas. In addition,

¹ COHPAC™ is an EPRI-licensed technology centered around the combination of an existing or new electrostatic precipitator with a high air-to-cloth ratio fabric filter.

the sorbent made the fly ash unacceptable for marketing as a concrete additive due to increased carbon content.

PG&E's Brayton Point Unit 1

Baseline tests conducted at the bituminous coal-fired Brayton Point Unit 1 showed “co-benefit” mercury removal ranging from 30 to 90 percent with the majority of capture occurring across the first CS-ESP. A carbon injection system installed between the two ESPs to compare “co-benefit” removal versus PAC injection showed greater than 90 percent total mercury capture with a PAC (DARCO[®]) injection concentration of 20 lb/million cubic feet (Mcf). Flue gas measurements indicated that PAC injection, coupled with HCl concentrations on the order of 150 ppm, promoted Hg⁰ capture. Testing at Brayton Point revealed that up to 90 percent of in-flight mercury capture occurs in less than a half of a second, which places these interactions upstream of the ESP.

PG&E's Salem Harbor Unit 1

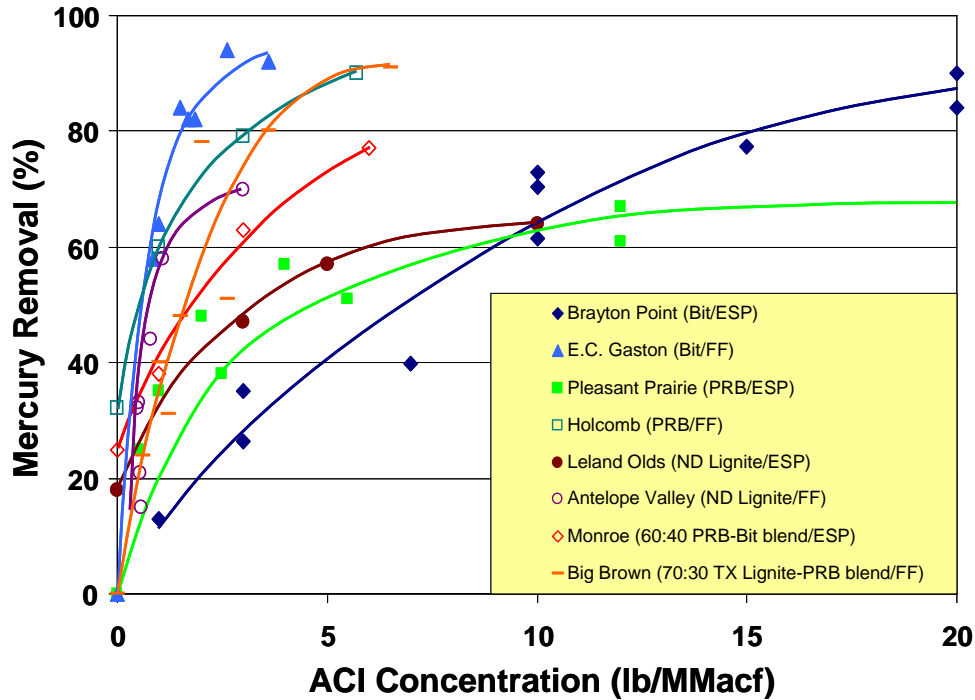
Field tests of PAC adsorption capacity as a function of temperature conducted at the bituminous coal-fired Salem Harbor Unit 1 showed that the amount of mercury removed deteriorated as the CS-ESP (474 SCA) inlet temperature was raised to 350°F, with maximum mercury removal of 45 percent. Tests exploring the impact of selective non-catalytic reduction (SNCR) on mercury removal showed mercury removal efficiencies ranging from 80 to 95 percent regardless of SNCR operation.

Southern Company's Plant Yates Unit 1

Untreated PAC injection tests, conducted over two, 30-day tests under a Phase II effort showed that RWE Rhinebraun's Super HOK sorbent achieved 50 to 60 percent total mercury capture, with injection rates ranging from 4.5 to 9.5 lb/MMacf at Plant Yates Unit 1. The effect of ACI on the unit's small-SCA (173 SCA) ESP and wet FGD operation showed an increase in the ESP arcing rate during continuous ACI, particularly at high load. The 30-day test caused no visible physical damage to the ESP, but it is unknown what effect the increased arcing rate will have on ESP performance over longer time periods.

DTE Energy's Monroe Station Unit 4

Thirty-day tests conducted at Monroe Station Unit 4 using DARCO[®] Hg showed mercury removal averaged 78 percent with an injection rate of 4.9 lb/MMacf. This unit burns a blend of 60 percent subbituminous (PRB) and 40 percent bituminous coal with an SCR and CS-ESP. A performance summary of DARCO[®] Hg during select Phase I and II full-scale field tests is shown in Figure 2.



* All data generated using NORIT Americas' DARCO® Hg

Figure 2. Phase I and II Performance Curves for Untreated ACI

2.3. CHEMICALLY TREATED PACS AND OTHER SORBENTS

Limited mercury removal achieved by untreated ACI spurred the development of chemically treated PACs. Two brominated PACs, NORIT Americas' DARCO® Hg-LH and Sorbent Technologies' B-PAC™ have consistently been top performers at Phase II field testing units burning lower-rank coals. Their outstanding performance has reduced the estimated cost of mercury control by reducing the ACI rate required to achieve a given level of control, which offsets the higher cost of these sorbents.

Great River Energy's Stanton Station Unit 10

With DARCO® Hg-LH injection at 0.7 lb/MMacf, total Mercury capture across the spray dryer absorber and fabric filter (SDA/FF) configuration at the North Dakota lignite-fired Stanton Station Unit 10 averaged 59 percent. However, greater than 90 percent mercury capture was achieved at this unit during parametric trials with both DARCO® Hg-LH and B-PAC™ injection at 1.5 lb/MMacf.

Sunflower Electric's Holcomb Station Unit 1

Total mercury capture averaged 93 percent across the SDA/FF configuration at the PRB coal-fired Holcomb Station with DARCO® Hg-LH injection at 1.2 lb/MMacf.

The need for chemically treated activated carbon in low-rank coal power plants was especially well demonstrated during testing of untreated DARCO[®] activated carbon at the PRB coal-fired Pleasant Prairie Unit 2 in 2001-2002. Mercury removal was limited to 65 percent in spite of activated carbon injection concentrations as high as 30 lbs/Mcf. This insufficient mercury removal was likely due to low halogen concentrations in the flue gas (HCl < 1 ppm). Additions of halogen (bromine) to the activated carbon proved to effectively and inexpensively increase mercury removal to acceptable levels.

At this time, there are at least six halogen-enhanced (brominated) or chemically treated sorbents available or under development. These are from Sorbent Technologies (B-PAC, C-PAC, H-PAC), NORIT America (DARCO Hg-LH), and Alstom-PPL (Mer-Clean 8, Mer-Clean 8-21).

Brominated sorbents cost more per unit volume than untreated activated carbon, but due to brominated sorbents having a higher mercury removal rate, the incremental cost of using brominated sorbents at low-ranked coal power plants is approximately one-half to one-seventh of the other sorbents tested.

DTE Energy's St. Clair Station Unit 1

At St. Clair (85:15 PRB and bituminous blend), 94 percent average total mercury removal was achieved across the CS-ESP with B-PAC[™] injection at 3 lb/MMacf.

AmerenUE's Meramec Station Unit 2

At the PRB coal-fired Meramec Station, 93 percent average total mercury removal was achieved across the CS-ESP with DARCO[®] Hg-LH injection at 3.3 lb/MMacf.

PacifiCorp's Dave Johnston Station Unit 3

A chemically treated Mer-Clean[™] 8 injection rate of 0.63 lb/MMacf achieved an average total mercury removal of 92 percent across the CS-ESP at the PRB coal-fired Dave Johnston Station.

Basin Electric's Leland Olds Station Unit 1

A chemically treated Mer-Clean[™] 8 injection rate of 1.4 lb/MMacf achieved an average total mercury removal of 90 percent across the CS-ESP at the North Dakota lignite-fired Leland Olds Station.

Progress Energy's Lee Station Unit 1

Total mercury capture averaged 85 percent across the CS-ESP at Lee with B-PAC[™] injection at 8 lb/MMacf. The 30-day long-term test at Lee Station was conducted with the sulfur trioxide (SO₃) flue gas conditioning (FGC) system idled and opacity levels remained acceptable.

Reliant Energy's Portland Station Unit 1

At the medium-sulfur (two percent) bituminous-fired Portland Station, about 95 percent average total mercury capture was observed with chemically treated Mer-Clean™ 8-21 injection at 8.5 lb/MMacf. The reduced efficiency of the Mer-Clean™ sorbents at Portland may have been caused by elevated levels of flue gas SO₃ resulting from the combustion of medium-sulfur bituminous coal.

Great River Energy's Stanton Station Unit 1 [FY 2007]

At GRE's PRB coal-fired Stanton Station Unit 1, URS Group observed 85 percent average total mercury removal across the CS-ESP with B-PAC™ injection at 1.7 lb/MMacf.

Rocky Mountain Power's Hardin Station [FY 2007]

Baseline mercury capture at the PRB coal-fired Hardin Station ranged from 20 to 30 percent across the SCR and SDA/FF configuration. During parametric testing, an injection rate of about 1 lb/MMacf was required to attain slightly more than 90 percent total mercury removal with DARCO® Hg-LH and Calgon Carbon's brominated FLUEPAC™-MC Plus. In addition, injection of a DARCO® Hg and FLUEPAC™-MC Plus mixture achieved 90 percent total mercury at 0.14 lb/MMacf, with a low KNX™ additive rate. Long-term field testing results are currently unavailable.

NRG Texas Power LLC's Limestone Station Unit 1 [FY 2007]

URS conducted Phase III field testing at NRG Texas Power LLC's Limestone Electric Generating Station Unit 1, which fires a 70:30 blend of Texas lignite and PRB coals and is equipped with a CS-ESP and wet FGD. Baseline mercury removal was highly variable ranging from about 5 to 50 percent. Since this unit markets its fly ash for reuse, two mercury control technologies designed to preserve ash quality were evaluated during parametric tests: low-ash impact sorbent injection and TOXECON II™. During injection upstream of the ESP, the brominated B-PAC™ and DARCO® Hg-LH sorbents performed similarly with about 90 percent ACI mercury removal at 2 to 3 lb/MMacf. Untreated DARCO® Hg also achieved 90 percent ACI mercury removal with injection at slightly less than 6 lb/MMacf. Injection of the "concrete-friendly" C-PAC™ sorbent at about 1.5 lb/MMacf resulted in approximately 73 percent ACI mercury removal. During parametric trials with the TOXECON II™ configuration, ACI mercury removal was limited to about 60 percent with DARCO® Hg and DARCO® Hg-LH injection at about 5 to 6 lb/MMacf. Note that DARCO® Hg-LH injection into the TOXECON II™ configuration took place with the unit firing 100 percent PRB coal. A two-month continuous injection test was completed with DARCO® Hg-LH injection at 2 lb/MMacf and preliminary results indicate that the project goal of 50 to 70 percent ACI mercury removal across the ESP was achieved. In addition, URS is confident that the low DARCO® Hg-LH injection rate will not prohibit fly ash reuse, but analysis is ongoing.

LCRA's Fayette Unit 3 [FY 2007]

A Phase III evaluation of Mer-Cure™ was completed at LCRA's Fayette Unit 3 in April 2007. Baseline mercury capture was approximately 50 percent across the CS-ESP and wet FGD. All

results are based on the incremental (or ACI) level of mercury control. Alstom-PPL evaluated three sorbents (eSorb™ 11, eSorb™ 13, and eSorb™ 18) designed to preserve fly ash quality, along with Mer-Clean™ 8, during parametric testing. Excluding eSorb™ 18, 80 percent ACI mercury capture was achieved with injection at 0.4-0.5 lb/MMacf. At an injection at about 0.8 lb/MMacf, eSorb™ 11 and Mer-Clean™ 8 attained 90 percent ACI mercury capture. Preliminary results indicate that fly ash remains marketable with eSorb™ 13 at about 0.5 lb/MMacf (85 percent ACI mercury capture). The testing program was halted prematurely due to an unscheduled plant outage.

2.4. TESTS WITH HIGH SO₃ FLUE GAS SITES

Conesville Station Unit 6

ADA-ES evaluated more than 50 candidate sorbents at the Conesville Station Unit 6 combusting high-sulfur (three to four percent) bituminous coal. These Phase II field tests showed total mercury removal was limited to approximately 30 percent with chemically treated PAC injection at 12 lb/MMacf. They also showed that flue gas SO₃, even at low concentrations, can interfere with the performance of ACI.

NETL research has shown that even low concentrations of flue gas (SO₃) can interfere with the performance of ACI. SO₃ is generated in coal combustion flue gas via three mechanisms:

- Oxidation of SO₂ within the furnace
- Further oxidation of SO₂ across SCR catalysts
- SO₃ FGC systems. It appears that SO₃ competes with mercury for adsorption sites on the PAC surface, thereby limiting its performance and/or requiring much higher ACI rates to achieve a given level of mercury control.

AmerenUE's PRB Coal-fired Labadie Station [FY 2007]

Turning off the Flue Gas Conditioning (FGC) at AmerenUE's PRB coal-fired Labadie Station increased total mercury removal from about 50 to 80 percent with a PAC injection at rate of 8 lb/MMacf. Greater than 90 percent mercury removal was observed with no SO₃ injection and DARCO® Hg-LH injection upstream of the air preheater at about 5 lb/MMacf. The performance of brominated B-PAC™ was also impacted by SO₃ FGC at Lee Station. With B-PAC™ injection at 8 lb/MMacf, mercury capture increased from 32 to 82 percent when SO₃ FGC was idled at Lee. One possible solution to this problem is the co-injection of PAC and alkaline materials. Preliminary results from a few Phase II field testing sites are encouraging.

Public Service of New Hampshire Company's Merrimack Station Unit 2 [FY 2007]

ADA-ES is conducting a Phase III field test at Public Service of New Hampshire Company's Merrimack Station Unit 2, which utilizes a cyclone-fired boiler to burn a blend of bituminous

coals (1.0 to 1.3 percent sulfur content) and is equipped with an SCR system followed by two CS-ESPs in series. This is a challenging environment for ACI due to elevated SO₃ levels and high flue gas temperature. During parametric testing, several mercury sorbents were evaluated both with and without the injection of magnesium oxide (MgO) or sodium sesquicarbonate (trona)—two potential SO₃ mitigation additives that also permit a reduction in flue gas temperature. Results indicate that trona injection enhanced ACI performance to a greater degree than MgO; however, the sodium content of trona may limit fly ash recycling opportunities.

Without SO₃ mitigation, mercury removal was limited to about 22 percent with chemically treated ACI at 8 lb/MMacf. Untreated DARCO[®] Hg injection at 8 lb/MMacf, coupled with trona injection, resulted in about 65 percent mercury removal. During a short-term experiment, 90 percent mercury removal was observed with milled (to less than 15 microns) trona injection upstream of the air pre-heater at 500 lb/hr and brominated DARCO[®] Hg-LH injection between ESP1 and ESP2 at 6 lb/MMacf. ADA-ES will attempt to replicate this high performance and evaluate the impact of ACI, coupled with SO₃ mitigation, on fly ash utilization and stack opacity during a two to three-month long-term test scheduled to begin October 2007.

2.5. FULL-SCALE FIELD TESTS OF TECHNOLOGIES DESIGNED TO PRESERVE FLY ASH RECYCLING

Luminant Power's Big Brown Station Unit 2

Under the Phase II program, NETL has also funded a full-scale field test of the TOXECON[™] configuration at Luminant Energy's Big Brown Unit 2, which fires a 70 percent Texas lignite and 30 percent PRB coal blend. The University of North Dakota Energy & Environmental Research Center (UNDEERC) evaluated the performance of untreated ACI, co-injection of sorbent enhancement additive (SEA) and untreated PAC, and UNDEERC's proprietary enhanced PAC during parametric tests. Due to concerns about the cumulative impact of SEA and PAC injection on differential pressure across the relatively small FF (air-to-cloth ratio of 12:1), UNDEERC's enhanced PAC was selected for the 30-day long-term demonstration. Total mercury capture averaged about 74 percent with an injection rate of 1.5 lb/MMacf.

According to an in-depth balance-of-plant (BOP) analysis performed by UNDEERC, enhanced PAC injection at 1.5 lb/MMacf increased the pressure drop across the FF at Big Brown by about 1-inch H₂O at high load (~600 MW). Handling and storage issues with the PAC/ash mixture have also been observed at both Presque Isle and Big Brown. In particular, a portion of the PAC/ash mixture was found to be very hot and smoldering at each unit. Preliminary results indicate the need to monitor and empty the FF hoppers on a regular basis to avoid self-heating and ignition of the PAC/ash mixture.

Entergy's Independence Station Unit 1 [FY 2007]

A full-scale TOXECON II[™] field test conducted by ADA-ES at Entergy's PRB coal-fired Independence Station Unit 1 showed about 60 percent average total mercury removal with DARCO[®] Hg-LH injection at 4 to 5 lb/MMacf. Therefore, a subsequent full-scale field test conducted at Independence in February 2007 with DARCO[®] Hg-LH injection at 5.5 lb/MMacf achieved 90 percent total mercury removal. The TOXECON II[™] technology injects sorbents

directly into the downstream collecting fields of an ESP. Since the majority of fly ash (~90 percent) is collected in the upstream ESP fields, only a small portion of the total collected ash contains spent sorbent. The technology requires minimal capital investment compared with the TOXECON™ configuration and no retrofit FF is required.

Duke Energy's Miami Fort Station Unit 6

The performance of Amended Silicates™ non-carbon sorbent (comprised of a chemically-amended silicate substrate), evaluated during a 30-day field test at Duke Energy's medium-sulfur (~2.3 percent) bituminous-fired Miami Fort Unit 6, showed that total mercury capture across the CS-ESP (353 SCA) averaged 40 percent with an injection rate of 5-6 lb/MMacf. Once again, flue gas SO₃ may have had a detrimental effect on sorbent performance at Miami Fort.

Midwest Generation's Crawford Station Unit 7 [FY 2007]

Sorbent Technologies' 30-day evaluation of brominated, "concrete-friendly" C-PAC™ at Midwestern Generation's PRB coal-fired Crawford Station Unit 7 showed 81 percent total mercury removal across the small CS-ESP with an injection rate of 4.6 lb/MMacf. Preliminary results indicate that fly ash samples collected during sorbent injection at these units would satisfy the criteria for reuse in concrete production.

2.6. MERCURY CO-REMOVAL ACROSS WET FGD SYSTEMS USING CATALYTIC MERCURY OXIDATION

Great River Energy's Coal Creek Station

URS Corporation, in collaboration with EPRI, Great River Energy, City Public Service of San Antonio, and the North Dakota Industrial Commission, conducted pilot-scale testing of several different Hg⁰ oxidation catalysts composed of palladium, tire-derived activated carbon, subbituminous ash, and selective catalytic reduction (SCR) catalysts at a North Dakota lignite-fired plants. After 13 months of operation, the carbon catalyst showed 79 percent mercury oxidation. After 20 months of operation, the palladium catalyst showed 67 percent oxidation. The SCR and subbituminous ash catalysts showed significantly lower activity. The palladium catalyst could be thermally regenerated to increase its oxidation activity from 67 to 88 percent.

Luminant Power's Monticello Station Unit #3

Four mercury oxidation catalysts (gold, SCR catalyst, regenerated palladium, and fresh palladium) installed downstream of the CS-ESP at TXU's Monticello Station Unit 3 showed severe fly ash buildup on the catalyst surfaces, likely caused by frequent pilot unit outages during the test campaign. Following in-situ catalyst cleaning in August 2006, Hg⁰ oxidation was approximately 72 percent across the regenerated palladium catalyst and 66 percent across the gold catalyst, after 17 months of pilot-scale operation. Tests completed in April 2005 indicated total mercury capture across a pilot-scale wet FGD ranged from 76 to 87 percent, compared with only 36 percent removal under baseline conditions.

Southern Company's Plant Yates Unit 1 [FY 2007]

Pilot-scale tests of catalytic mercury oxidation installed downstream of a CS-ESP using fresh palladium, gold, and regenerated SCR catalysts showed 58 percent Hg^0 oxidation across the fresh gold catalyst, 38 percent across the fresh palladium catalyst, 32 percent across the regenerated SCR catalyst, and 26 percent across the regenerated gold catalyst after 10 months of operation.

2.7. CHEMICAL ADDITIVES FOR ELEMENTAL MERCURY OXIDATION

Chemical additives such as calcium chloride (CaCl_2), magnesium chloride (MgCl_2), and proprietary formulations promote flue gas Hg^0 oxidation and enhance FGD mercury capture. The additives are sprayed onto the pre-combusted coal as an aqueous salt solution. This approach facilitated the capture of mercury by maximizing the residence time available for interactions with Hg^0 with the elements.

Minnkota Power's Milton R. Young Unit 2

UNDEERC evaluated three additives during short-term parametric tests: SEA1, CaCl_2 ; SEA2, a proprietary chemical formulation; and MgCl_2 at this unit that fires North Dakota lignite coal in a cyclone boiler and is equipped with a CS-ESP and wet FGD. SEA2 yielded highest results, achieving approximately 44 percent total mercury capture across the ESP/FGD combination with injection at 75 ppm (on a dry coal basis), as compared with less than 20 percent mercury capture with SEA1 and MgCl_2 injection at 500 ppm. About 60 percent total mercury capture was observed with SEA2 injection at 50 ppm (on a dry coal basis), coupled with untreated DARCO[®] Hg injection at 1 lb/MMacf. During the 30-day test, total mercury capture across the ESP/FGD ranged from 50 to 65 percent with SEA2 injection at 60-100 ppm (on a dry coal basis) and DARCO[®] Hg injection at 0.15 lb/MMacf.

Luminant Power's Monticello Station Unit 3

Parametric testing at MoSES Unit 3 burning Texas lignite and PRB coals evaluated the performance of CaCl_2 and calcium bromide (CaBr_2). These trials clearly displayed the superior performance of CaBr_2 as 72 percent Hg^{2+} was captured at the ESP outlet with an injection rate of 100 ppm bromine (Br) in the coal (on a dry basis). As a result, long-term testing was conducted with CaBr_2 . The two-week test, at a CaBr_2 injection rate of 55 ppm Br in the coal, oxidized 67 percent of the mercury entering the FGD, resulting in an average total mercury capture of 65 percent. At a CaBr_2 injection rate of 113 ppm bromine in the coal, Hg^0 oxidation reached 85 percent, resulting in an average total mercury capture of 86 percent over the two-week test. In addition, a short-term test conducted with a CaBr_2 injection rate of 330 ppm bromine in the coal resulted in 92 percent total mercury capture across the ESP/FGD.

2.8. FGD ADDITIVES

Hg^0 re-emissions have been observed at several coal-fired units and occur when Hg^{2+} captured by a wet FGD is chemically reduced within the vessel and re-emitted as Hg^0 . Chemical models suggest that Hg^0 re-emissions in full-scale wet FGD systems could be greatly influenced by factors such as chloride concentration and slurry droplet pH. This was further evaluated by full-

scale field testing of FGD additives to inhibit the partitioning and re-emission of mercury from FGD byproducts.

Plant Yates Monticello Unit 3, Petersburg Station [FY 2007]

URS conducted pilot and full-scale field tests of a wet FGD additive (Degussa Corporation's TMT-15) to determine whether the additive can precipitate mercury as a stable salt, thereby minimizing Hg^0 re-emissions and lowering FGD liquor mercury concentrations. This project is also assessing whether this same additive can be used to minimize mercury in FGD used as synthetic gypsum through the separation of the fine mercury-containing salts from the remainder of the byproduct. Full-scale field tests at Indianapolis Power & Light's Petersburg Station Unit 2 and Plant Yates have been inconclusive and below expectations.

Recently, URS completed a 30-day full-scale test at Plant Yates in September 2007 using a wet FGD additive developed by Nalco Company. The results of this test will be presented at the DOE Mercury Control Technology Conference scheduled for December 2007 in Pittsburgh, PA.

2.9. OTHER TECHNOLOGIES - MULTI-POLLUTANT CONTROL TECHNOLOGIES

Allegheny Power's Mitchell Power Station

CONSOL, Allegheny Energy, Alstom Power, Environmental Elements, and Carmeuse North America conducted a pilot-scale evaluation of Low-Temperature Mercury Control (LTMC). This process controls mercury by cooling the flue gas temperature to approximately 220 °F, which promotes adsorption on the unburned carbon in fly ash. Greater than 90 percent total mercury capture was achieved during the pilot-scale testing

2.10. CHARACTERIZATION OF MERCURY EMISSIONS VIA COMBUSTION MODIFICATION

Progress Energy's Lee Station Unit 3 [FY 2007]

General Electric Energy and Environmental Research Corporation evaluated a novel multi-pollutant control technology to reduce mercury, NO_x, and carbon monoxide emissions at Progress Energy's bituminous coal-fired Lee Station Unit 3 equipped with a cold side-ESP and SO₃ flue gas conditioning system. Preliminary results indicate a 38 percent improvement in "co-benefit" mercury capture following combustion optimization. Meanwhile, untreated carbon injection at about 18 lb/MMacf achieved 80 percent total mercury removal with SO₃ conditioning idled, but the removal efficiency was limited to approximately 55 percent with the operation of the SO₃ FGC system.

2.11. MERCURY CONTROL TECHNOLOGIES

Cost Analysis [FY 2007]

NETL recently completed an updated economic analysis of mercury control, based on data from 12 test sites utilizing three carbon injection variations (conventional activated carbon, chemically treated activated carbon, and conventional activated carbon combined with an SEA applied to the coal).

The economic analyses were conducted on a plant-specific basis. Analyses were completed in a manner that yields the cost required to achieve low (50 percent), medium (70 percent), and high (80 to 90 percent) levels of mercury control “above and beyond” the plant-specific baseline mercury removal. A data adjustment methodology was developed to account for the level of baseline mercury capture observed and to incorporate the average level of mercury removal measured during the long-term continuous carbon injection trial. These analyses were carried out to provide NETL with a metric to gauge its success in achieving the target of reducing baseline mercury control costs by 25 to 50 percent. Mercury control cost estimates were presented for the three carbon injection variations. Chemically treated carbon injection and SEA coal treatment are intended to compensate for the lack of naturally occurring halogens in the combustion flue gas of low-rank coals, because halogens appear to limit the mercury capture efficiency of conventional carbon injection. For this reason, conventional carbon injection cost estimates were not conducted for subbituminous or lignite coals.

Tables 1, 2, and 3 provide plant specific cost estimates for three levels of mercury removal due to carbon injection at the twelve test sites. The sites burning subbituminous and lignite coal were all tested with either chemically treated PAC or conventional PAC and coal treated with CaCl₂. Some of the costs are impacted by plant specific factors such as the incremental costs at Yates and Lee being higher than Monroe and Portland in Table 1 due to low inherent mercury content in the coal at Lee and the high baseline removal of mercury at Yates. Another trend of note can be seen in Table 2 where the incremental cost of 70 percent mercury removal is lower than 50 percent due to the increase in mercury captured outpacing the increased cost of mercury control.

The capital costs for activated carbon injection are expected to be fairly uniform and independent of plant size. This implies that capital costs on a per-kilowatt basis will be higher for smaller plants, indicating that large power plants will have an economic advantage over smaller plants. The total capital requirement for power generation units in the updated economic analyses ranges between \$1.3 million and \$1.9 million (2006 dollars) except for one particularly large unit (Monroe Unit 4), which had capital costs of \$3 million. Capital costs included the following:

- Uninstalled equipment cost (e.g., bulk storage silo, pneumatic conveying systems, foundations, distribution manifold, injection lances, etc.).
- Materials and labor associated with site integration (e.g., electrical supply upgrades, process control integration, instrument air, adequate lighting, etc.).
- Sales tax of 6 percent

Table 1. 20-Year Levelized Cost of Mercury Control for Bituminous Units

Plant (Sorbent)	Byproduct Impacts	50% carbon injection mercury removal			70%			80%-90%		
		Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed
Yates Unit 1 (Super HOK)	Without	3.85	0.98	55,200	8.98	1.72	69,500	N/A		
	With		2.92	165,000		3.66	148,000			
Monroe Unit 4 (Darco® PAC)	Without	1.46	0.38	17,200	3.38	0.75	24,000	5.78	1.20	33,800
	With		1.62	73,100		1.99	63,900		2.45	68,800
Lee Unit 1 (B-PAC™)	Without	2.07	1.14	71,400	4.83	1.95	87,200	8.27	2.95	103,000
	With		2.85	179,000		3.66	164,000		4.67	163,000
Portland Unit 1 (Mer-Clean™ 8-21)	Without	0.59	0.45	13,400	1.39	0.69	14,900	5.34	1.94	32,300
	With		1.60	47,900		1.84	39,600		3.09	51,500

Table 2. 20-Year Levelized Cost of Mercury Control for PRB Units

Plant (Sorbent)	Byproduct Impacts	50% carbon injection mercury removal			70%			80%-90%		
		Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed
Holcomb Unit 1 (DARCO® Hg-LH)	Without	0.11	0.15	4,380	0.27	0.18	3,910	1.03	0.37	6,090
	With		0.86	25,600		0.89	19,000		1.08	17,900
St. Clair Unit 1 (B-PAC™)	Without	0.26	0.39	17,200	0.60	0.52	16,300	2.31	1.16	28,500
	With		1.36	60,500		1.49	47,200		2.13	52,500
Meramec Unit 2 (DARCO® Hg-LH)	Without	0.27	0.38	12,200	0.62	0.48	11,100	2.40	0.99	17,800
	With		1.74	56,100		1.84	42,400		2.35	42,100
Dave Johnston Unit 3 (Mer-Clean™ 8)	Without	0.06	0.26	7,440	0.14	0.30	5,970	0.55	0.46	7,190
	With		1.55	44,000		1.59	32,100		1.75	27,500
Stanton Unit 1 (B-PAC™)	Without	0.41	0.39	16,700	0.95	0.54	16,500	3.65	1.29	30,500
	With		1.07	45,400		1.22	36,900		1.97	46,400

Table 3. 20-Year Levelized Cost of Mercury Control for ND Lignite Units

Plant (Sorbent)	Byproduct Impacts	50% carbon injection mercury removal			70%			80%-90%		
		Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed	Carbon Injection lb/MMacf	COE Increase Mills/kWh	\$/lb Hg Removed
Leland Olds Unit 1 (Darco® Hg & CaCl ₂)	Without	2.15	0.74	18,300	5.04	1.21	21,500	8.65	1.81	24,900
	With		3.37	83,600		3.84	68,200		4.44	61,200
Stanton Unit 10 (DARCO® Hg-LH)	Without	0.49	0.85	20,300	1.15	1.05	17,900	1.98	1.30	17,300
	With		2.58	61,500		2.78	47,300		3.03	40,100
Leland Olds Unit 1 (Mer-Clean™ 8)	Without	0.18	0.32	7,900	0.42	0.42	7,400	1.64	0.91	12,600
	With		2.95	73,200		3.05	54,100		3.54	48,900

3. COAL UTILIZATION BY-PRODUCTS

3.1. SUBPROGRAM SUMMARY

Developing more beneficial uses for coal utilization by-products (CUB) will improve power generation economics, conserve natural resources and landfill space, and reduce carbon dioxide (CO₂) emissions. These by-products are formed during the combustion of coal for electric power generation. The focus of this subprogram of the IEP Program is to support the environmentally safe and technically sound handling of CUB material, with the goal of increasing CUB use in construction and other industries. Research activities explore the environmental impacts of CUB disposal versus utilization, the optimization of utilization methods, and the collection and dissemination of data to assist in CUB-related regulatory decisions. Many of the CUB projects at NETL are being conducted through consortia described later in this section.

Some of the more successful CUB applications include its use as a partial substitute for cement in concrete (fly ash), structural fill material (bottom ash and fly ash), blasting grit (boiler slag), and in the manufacture of wallboard (FGD gypsum). Several types of CUB are used in mine reclamation applications, in particular fluidized-bed combustion (FBC) ash, whose alkaline properties make the ash useful in the remediation of acidic mine backfills.

3.2. DEVELOPMENT OF ADVANCED TECHNOLOGIES TO EXPAND MARKET USE FOR COAL COMBUSTION BY-PRODUCTS

Market Assessment/Demonstration of Lignite FBC Ash Flowable Fill Applications

FBC ash from lignite cannot be used in conventional ash applications such as ready-mix concrete. R&D conducted by the Western Research Institute resulted in a cost-effective flowable fill product (Ready-Fill) for excavatable and structural applications. Ready-Fill utilizes ash from the lignite-fired Heskett plant, waste sand fines, and small amounts of cement and water. A total of seven full-scale field applications demonstrated the use of Ready-Fill for structural, excavatable, and niche applications, including a structural base for the coal unloading facility at Heskett power plant, an excavatable trench bedding for utilities, erosion control, and as base material for residential patios. The product is now commercially marketed in the Bismarck-Mandan area of North Dakota, where it is sold wholesale to concrete suppliers.

Ash-Based Grout Injection for Subsidence Control at Shamrock Mine

An ash-based grout has been developed that can be injected into flooded underground mines with minimal dispersion of the grout into water. The ash-based grout meets the stipulated ASTM strength requirements for grout based on the results of a systematic durability study that used a variety of manufactured aggregate and aggregate products that were produced using high loss-on-ignition (LOI) ash with a binder or FBC ash.

Advanced Technologies for the Separation of Carbon from Fly Ash

The University of Kentucky has developed an organic dispersant that can separate unburnt carbon from fly ash where fine sizes of ash may be recovered for use as a polymer filler or as a specialized, high-value cement additive. A unique hydraulic classifier was developed for this

application together with the design of a mobile pilot plant. Six different fly ashes have been fully evaluated and characterized chemically and physically, from which a model was developed for the hydraulic classification process.

3.3. CUB ENVIRONMENTAL RESEARCH

The goal of CUB environmental research is to characterize the environmental acceptability of these products and to understand the fate of mercury and other trace metals in these materials.

Characterize the Fate of Mercury in CUB

Using a Toxicity Characteristic Leaching Procedure (TCLP), Consol Technologies showed that mercury did not leach from coal, bottom ash, fly ash, spray dryer/FF ash or forced oxidation gypsum (FOG) in concentrations greater than the detection limit of the TCLP method (currently 1.0 ng/mL). This was true even with fly ash samples collected from the ESP during activated carbon injection for mercury control.

Mercury was detected at low concentrations in acidic leachates from all of the fixated and more than half of the unfixated FGD sludge samples. However, mercury was not detected in leachates from any sample when deionized (DI) water was the leaching solution.

Volatilization tests showed no mercury loss from fly ash, spray dryer/FF ash, unfixated FGD sludge, or forced oxidation gypsum (FOG). The mercury concentration of these samples all increased, possibly due to absorption from ambient surroundings. Mercury loss of 18 to 26 percent was detected after 3 and 6 months at 100°F and 140°F, respectively, from samples of the fixated FGD sludge.

Mercury was not detected in water samples collected from monitoring wells around an active FGD disposal site or an active fly ash slurry surface impoundment.

Leaching Volatilization and Microbial Testing of CUB in Disposal and Utilization Applications

UNDEERC has shown that five of the six CUB analyzed acted as mercury absorbents (or sinks), although a small amount may be released on storage. The previously reported value of a maximum of 0.26 grams of mercury release from 200,000 tons of ash may be revised with further data.

Frontier Geosciences - Determining the Fate of Hg in Fly Ash [FY 2007]

Beginning with the Phase I full-scale field testing program, NETL has required that field contractors evaluating Hg control via sorbent injection collect and analyze fly ash samples. Fly ash analyses are focused on determining the stability and ultimate fate of Hg during potential utilization applications and disposal. More recently, NETL awarded a contract to Frontier Geosciences, Inc. to conduct independent laboratory analysis of CUB generated during the NETL Phase II full-scale Hg control technology field testing program. The purpose of the independent laboratory analysis is to ensure that accurate and consistent laboratory procedures are used to determine the environmental fate of Hg in CUB. The Office of Research and

Development (ORD) within NETL has also been conducting in-house leaching experiments with fly ash collected from ACI field testing sites.

The Frontier work includes leaching studies using the Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312), low (40 °C for 30 days), medium (190 °C for 1 hour), and high-temperature (900 to 1200 °C for 5 minutes) Hg volatility tests, microbial methylation experiments, and halide analysis. Preliminary SPLP results indicate that little to no Hg would be released under normal disposal conditions. In addition, Hg bound to PAC sorbents, particularly those that have been chemically treated, appears to be more stable than the UBC-bound Hg. During the low-temperature volatility tests, essentially no Hg was emitted from the fly ash samples. Thermal desorption of Hg has been observed during the medium and high-temperature volatility tests conducted by Frontier; however, the extent of release is still under investigation.

Using a pure culture of sulfate reducing bacteria known to methylate Hg, the production of methyl-mercury over a 30 day period is being monitored to assess the methylation potential of Hg present in CUB. Preliminary results from this “worst-case-scenario” microbial mobilization study indicate an increase in methyl-mercury production. However, microbial activity has also stabilized a number of target metals.

3.4. INDUSTRY COLLABORATIVES

Combustion By-Products Recycling Consortium

The Combustion By-Products Recycling Consortium (CBRC) is an industry-based group formed to help develop and demonstrate technologies to address issues related to the recycling of CUBs. Several new applications have been developed, including the use of CUBs in paving bricks, composite wall panels, and foundry sand molds in commercial projects. Other CBRC technologies, such as fly ash-based sorbents for mercury control from power plant flue gas, have been selected for large-scale field demonstrations.

Coal Ash Resources Research Consortium

The use of sulfite-rich FGD by-products in agricultural applications is negatively impacted by the conversion of sulfite to sulfate. A Coal Ash Resources Research Consortium (CARRC) research project examined the kinetics for the conversion of sulfite in FGD by-products to sulfate and the conditions that facilitate the conversion. Results indicated chemical composition variability among the different samples as expected. Strength development tests indicated that all samples met the maximum water requirement limit, but only one sample, an FGD-SDA material, achieved adequate strength at 28 days to meet the strength activity index specification. All samples exhibited expansion, and evaluation of those data continues.

CARRC completed a 4-year study on the release of absorbed mercury by Coal Combustion By-Products (CCBs). The conclusions of this study showed that the presence of activated carbon with fly ash may increase the temperature at which mercury is released when CCBs are exposed to elevated temperature. Mercury is not readily released at temperatures below 250°C. Laboratory data indicated that the potential for ambient temperature vapor-phase mercury releases are unlikely to impact atmospheric mercury loading.

Coal Combustion Products Partnership

The Coal Combustion Products Partnership (C2P2), a collaboration with industry and EPA's Office of Solid Waste, focuses on the expanded use of improved CUB materials for a variety of high-volume industrial and medium-volume commercial applications. High-volume applications include highway construction uses, while medium-volume uses are in cement and concrete, air-cooled condenser (ACC) building blocks, and high-technology mineral extraction processes. Highway demonstration projects in Georgia, Pennsylvania, Delaware, North Dakota, Michigan and Kansas have not shown any cases of negative impact on groundwater quality as a result of coal ash use in highway applications.

3.5. NETL OFFICE OF R&D

Leaching Test Methodologies

R&D conducted by NETL's Office of R&D suggests that the leachates of Class F fly ash undergo a sharp drop in pH when the alkalinity of the ash is depleted and that the release of metal begins right after the drop in pH commences. Consequently, predicting (or preventing) the release of metals from fly ash depends on knowing when the fall in pH occurs. The final determination of a system to monitor leaching progress will depend upon the nature of the operation and the experience of the personnel involved.

Fate of Mercury in Ash and FGD By-Products

Long-term leaching tests with several leachants covering a broad pH range indicate that mercury captured on fly ash is stable. Less than one percent of the amount of mercury in the samples tested was extracted, even under acid or basic conditions that exceeded those found in nature. From some samples, mercury was more extractable at high pH. The cumulative release of mercury was not related to the source of the samples or to the concentration of mercury. The amount of carbon, either as unburned carbon from the coal or as activated carbon injected in control tests, could not be directly correlated to the release of mercury. Although the results of these leaching tests did not clarify the factors that control the release of mercury from fly ash, they indicate that mercury in fly ash is very stable.

4. WATER-ENERGY INTERFACE

4.1. SUBPROGRAM SUMMARY

Each kilowatt-hour of electric power generated via a thermal process involving fossil fuels requires the withdrawal of approximately 25 gallons of water (weighted average for all thermoelectric power generation) used primarily for cooling and secondarily for the operation of FGD units, ash handling, wastewater treatment, and wash water. According to the United States Geological Survey, thermoelectric generation accounted for 39 percent (136 billion gallons per day [BGD]) of all freshwater withdrawals in the Nation in 2000, which is second only to irrigation. Studies conducted by NETL estimate that 6.2 BGD of freshwater was consumed by thermoelectric plants in 2005. In addition to the significant amount of water needed for the

generation of electricity, power plants may also impact water quality. Of particular concern is the deposition of trace quantities of air pollutants into water systems. The IEP Water-Energy Interface is focused on developing an understanding of the impacts of electricity production on water quantity and quality and on research, development, and demonstration of technologies to minimize any negative impacts of freshwater use in power plants. The program is built around four specific areas of research:

- Non-Traditional Sources of Process and Cooling Water
- Innovative Water Reuse and Recovery
- Advanced Cooling Technology
- Advanced Water Treatment and Detection Technology

4.2. NON-TRADITIONAL SOURCES OF PROCESS AND COOLING WATER

Specific research categories in Non-Traditional Sources of Process and Cooling Water are mine water, oil and gas produced water, municipal waste water, high total dissolved solids (TDS), ground water, and ash pond effluent. Table 4 provides summary information on participating researchers and a brief description of their projects in this category.

Table 4. Participating Research Organizations and Project Descriptions	
Researcher	Project Description
West Virginia University Water Research Institute	Assess the feasibility of underground mine water in the Northern West Virginia and Southwest Pennsylvania as a source for cooling water for power plants.
West Virginia University Water Research Institute [FY 2007]	Under wet and dry conditions, locate, sample, and determine flow of mine discharges around the 300 MW Beech Hollow, Southwestern Power Administration power plant. Develop a computer-based design tool for estimating the cost of water acquisition and delivery to the power plant.
EPRI	Collect, treat (to lower the total dissolved solids), and transport oil and gas produced water to the 1,800 MW San Juan Generating Station for use as makeup water for the power plant cooling system.
Nalco Company [FY 2007]	Using produced/reclaimed municipal wastewater to establish quantitative technical targets, develop scale inhibitor chemistries for high stress conditions, and determine the feasibility of membrane separation technologies to minimize scaling. Develop selected separation processes.
University of Pittsburgh, Carnegie Mellon University [FY 2007]	Determine the feasibility of using secondary treated municipal wastewater, passively treated coal mine drainage, and ash pond effluent waters in coal-fired power plants.

Mine Water

Eight potential sites where underground mine water is available in sufficient quantity to support the 4,400 gallon per minute (gpm) makeup water requirements for a closed-loop 600 MW plant were identified. Of these, three were further evaluated for a preliminary design and cost analysis of mine pool water collection, treatment, and delivery to a power plant. One of the three sites was selected for each of the three mine pool water chemistry categories based on “net alkalinity”

as measured in a milligrams per liter (mg/L) equivalent concentration of calcium carbonate (CaCO₃). These categories are net acidic (<-50 mg/L), neutral (-50 to +50 mg/L), and net alkaline (>+50 mg/L). From Table 5, it was concluded that, depending on site conditions and water treatment requirements, utilization of mine pool water as a source of cooling water makeup can be cost competitive with freshwater makeup systems.

Table 5. Cost Analysis Summary			
Cost	Flaggy Meadows (net-acidic)	Irwin (near-neutral)	Uniontown (net-alkaline)
Total Capital Cost, \$	5,740,000	3,770,000	3,464,000
Operating Cost, \$/year	1,367,000	363,000	433,000
Annualized Cost, \$/1,000 gallons	0.79	0.26	0.29

Oil and Gas Produced Water

A comprehensive study on the feasibility of using water produced from oil and gas wells in the San Juan Basin as process water for the San Juan Generating Station in Farmington, NM showed that the most economical method was to use high-efficiency reverse osmosis with a brine concentrator distillation unit to process the approximately 1,100 gpm of water needed by the power plant. Major barriers to using water from this location are water quality (salinity, or TDS) and that the water sources are dispersed over a large area. A pipeline was determined to be the most efficient method to gather and convey the water to the power plant.

4.3. INNOVATIVE WATER REUSE AND RECOVERY

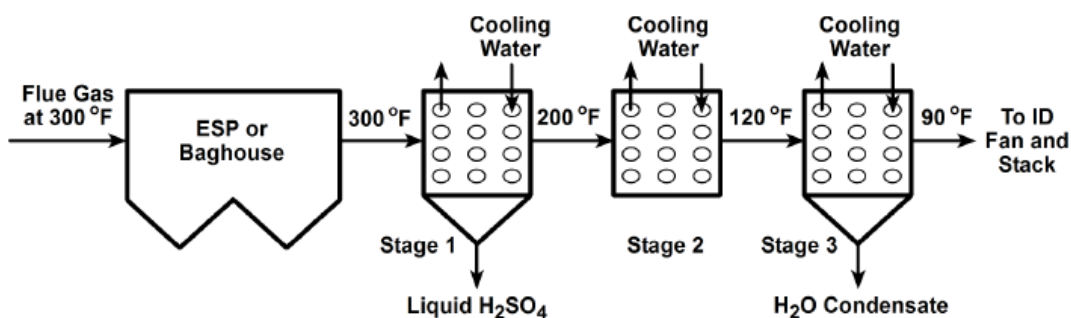
Specific research categories in Innovative Water Reuse and Recovery are the recovery of water from flue gas, waste heat from condenser cooling water for coal drying, use of condenser waste heat to produce freshwater from saline water, and evaporative loss reduction from flue gas. The research focus is on developing advanced technologies to reuse power plant cooling water and associated waste heat and on investigating methods to recover water from coal and power plant flue gas. The goal is to reduce fossil fuel power plant water withdrawal and consumption. Table 6 provides additional information on participating researchers and their project descriptions.

Table 6. Participating Research Organizations and Project Descriptions	
Researcher	Project Description
UNDEERC [FY 2007]	Develop a liquid desiccant-based dehumidification system that can remove water vapor from combustion flue gas efficiently and economically.
Lehigh University and Great River Energy	Evaluate the performance and economic feasibility of using low-grade power plant waste heat to partially dry low-rank coals prior to combustion.
University of Florida [FY 2007]	Use a diffusion-driven desalination (DDD) process in saline water to produce fresh water.
Lehigh University [FY 2007]	Evaluate the performance of a series of condensing heat exchangers to recover water vapor from power plant flue gas
URS Group [FY 2007]	Demonstrate the use of regenerative heat exchangers in reducing power plant flue gas temperatures to minimize evaporative water usage in wet FGD systems.

Recovery of Water from Flue Gas [FY 2007]

Given that thermal electric generation withdraws an average of 136 BGD, it becomes necessary to develop novel approaches to recover and reuse water from power plant flue gas, FGD systems, and coal drying systems. The benefits would be reduced freshwater withdrawal and consumption per kilowatt-hour of power production. So far, three candidate desiccants—lithium bromide, CaCl_2 , and triethylene glycol were tested and bench-scale. Based on test results, CaCl_2 was selected for initial pilot-scale testing. Results indicate that the performance of the system was better than predicted by chemical process models. Water removal from the flue gas ranged from 23 to 63 percent by volume, with the process conditions dictating the percentage of moisture removed. Although higher percentages of moisture removal requires higher energy inputs for heating and cooling, there were process conditions with little or no external heating or cooling that could potentially remove a significant volume of water from the flue gas. Extracted water quality was comparable to that produced in a reverse osmosis system. Off-gas of undesirable species from the water was minimal.

A pilot-scale, three-stage condensing heat exchanger system has been designed where the high-temperature section will reduce flue gas temperature from over 300 °F to an exit temperature of 200°F. The intermediate heat exchanger stage, with inlet and exit flue gas temperatures of approximately 200 °F and 110 °F, will be used to remove additional sensible heat from the flue gas and serve as a buffer stage between the high-temperature and low-temperature sections. In the low-temperature section, temperatures will be lowered to below 90 °F, where the water condensate will be extracted. Once constructed, the condensing heat exchanger will be tested using flue gas slipstreams from an oil-fired boiler at Lehigh University and a coal-fired boiler at Alstom Power's research facility in Windsor, CT.



Multistage Heat Exchangers

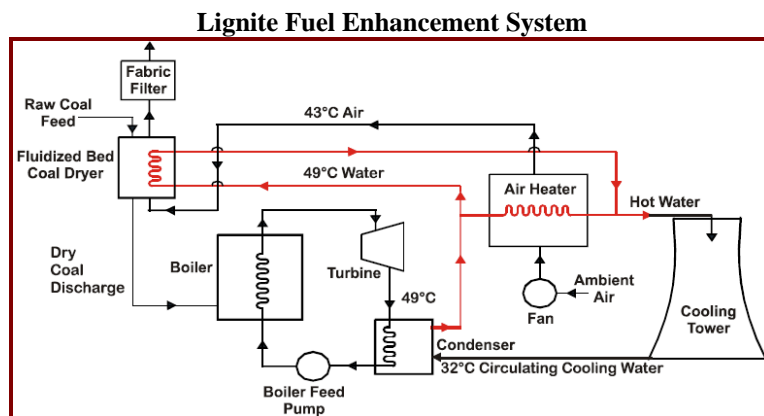
Figure 3. Multistage Heat Exchangers for Flue Gas Water Recovery

Waste Heat from Condenser Cooling Water for Coal Drying

Lehigh University completed bench-scale testing of fluidized-bed coal drying to develop mathematical models of the process. The models are being used by Great River Energy to

design, construct, and demonstrate the first coal dryer at the Coal Creek Station in a Clean Coal Demonstration Project. More than 100,000 tons of lignite was processed with its moisture content reduced from about 38.5 to 29.5 percent. Early estimates show that with just one pulverizer using dried coal, the stack flue gas flow rate from the Coal Creek unit decreased one percent, boiler efficiency increased 0.3 percent, pulverizer power consumption decreased 4.5 percent, sulfur oxide emissions fell 2.0 percent, NO_x emissions decreased 8.5 percent, and carbon dioxide emissions decreased 0.34 percent.

Test results for a lignite fuel enhancement system (LFES) show that as coal product moisture is reduced, boiler efficiency increases, net unit heat rate decreases, and the cooling tower makeup water requirements decrease for both the condenser cooling water (CCW) and CCW/FG drying systems (see table below). For a gross power generation of 572 MW and a 20 percent lignite product moisture, the station auxiliary power increases by 17 MW over the baseline for the CCW system and is relatively unchanged for the CCW/FG system. The relatively large increase in auxiliary power for the CCW system is caused by the large dryer and consequently high fluidization air flow rates needed by the low-temperature CCW drying system.



Results

	CCW	CCW/FG
Boiler Efficiency	+5.5%	+3%
Net Unit Heat Rate	-3.3%	-3.3%
Station Service Power	+17MW	Negligible
Cooling Tower Makeup Water	-380 gallons/minute	-140 gallons/minute

Use of Condenser Waste Heat to Produce Freshwater from Saline Water [FY 2007]

An economic simulation of an innovative diffusion-driven desalination (DDD) system using a laboratory-scale facility showed that the production costs of a DDD combined cycle power plant is very competitive compared with the costs required for reverse osmosis or flash evaporation technologies. Extensive measurements of the diffusion tower and direct contact condenser were made to validate performance. The analytical model of the diffusion tower was able to predict the thermal performance of counter flow packed beds with both air and water heating. In addition, the model of the direct contact condensers was able to predict the thermal performance

of both the co-current and counter-current flow packed beds. Based on the analysis performed, the waste heat from a 100 MW power plant can be used to produce 1.03 million gallons of freshwater per day using the DDD process.

Evaporative Loss Reduction from Flue Gas [FY 2007]

The approach in this application is to use regenerative heat exchange to reduce flue gas temperatures and thereby minimize evaporative water consumption in wet FGD systems. Although results are not available, a 50 percent reduction in the amount of water evaporated is expected. Other benefits of this project will include enhanced SO₃ emissions control via condensation on fly ash, improved ESP particulate control, mercury removal in the ESP, and avoided costs associated with flue gas reheat or wet stacks.

4.4. ADVANCED COOLING TECHNOLOGY

Specific research categories in Advanced Cooling Technology are; Wet Surface Air Cooler (WSAC), Ice Thermal Storage (ITS) for Cooling, Dry Cooling Systems Efficiency Improvement, and Air2Air Condensing Technology for Evaporative Water Loss Reduction. These research areas focus on developing technologies that improve performance and reduce costs associated with wet cooling, dry cooling, and hybrid cooling technologies. Table 7 provides additional information on participating researchers and a brief description of their projects in this category.

Table 7. Participating Research Organizations and Project Descriptions	
Researcher	Project Description
EPRI	Conduct pilot scale test of the WSAC as auxiliary cooling to determine its capacity to use low quality water for cooling at the San Juan Generating Station.
University of Pittsburgh	Perform an engineering analysis of two typical gas turbines at two locations for the ITS technology.
Ceramic Composites, Inc.	Develop a high thermal conductivity foam to be used as heat transfer medium in an ACC.
SPX Cooling Tech., Inc. [FY 2007]	Conduct pilot-scale testing of SPX’s Air2Air condensing technology in order to evaluate its effectiveness in reducing evaporative water loss in a cooling tower.
Drexel University [FY 2007]	Develop a self-cleaning metal membrane filtration system using electrical pulses to remove scale-forming ions from wet recirculating cooling systems.

Wet Surface Air Cooler

A Wet Surface Air Cooler (WSAC) pilot unit, operated for 2,898 hours at an equivalent of 24 to 70 cycles of concentration (based on freshwater fed to the cooling towers) showed no visible scale on the heat transfer surfaces (tube externals) and cooling was sustained throughout the test period. However, solids did build up at various places in the test unit; therefore, solids management (some type of filtration) will be necessary to use this technology. It does show promise for a method to use degraded water and reduce the volume of wastewater discharged.

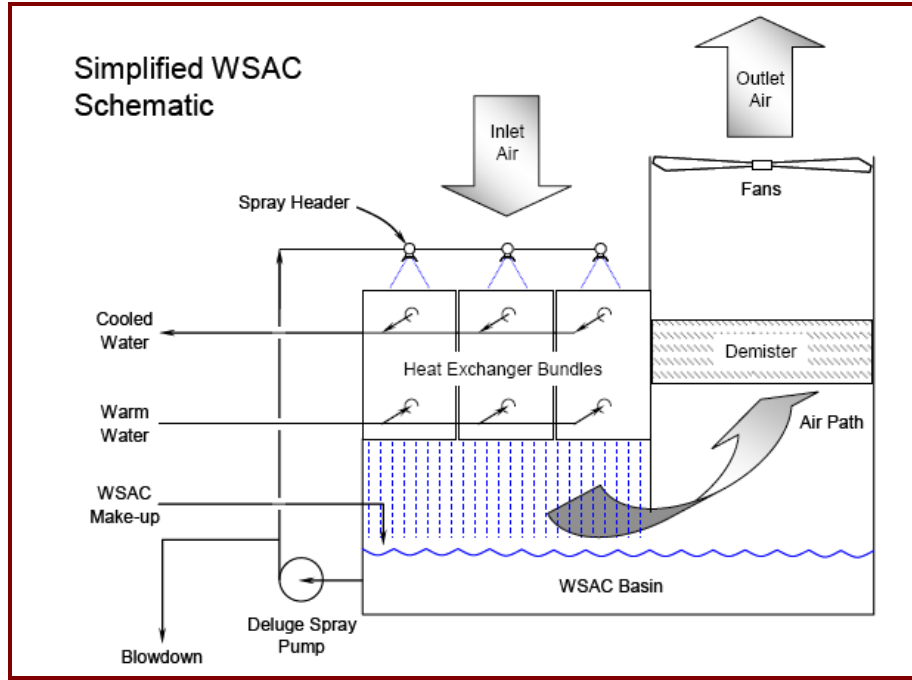


Figure 4. Simplified Schematic of a Wet Surface Air Cooler

Ice Thermal Storage for Cooling

A theoretical analysis and computer simulation of two case scenarios—hot and arid ambient conditions (Phoenix, AZ), and hot and humid conditions (Houston, TX)—designed to analyze the use of ITS technology to provide intake air cooling for gas turbines showed that significant improvement in both power output and efficiency can be achieved for an aero-derivative and an industrial gas turbine by using the ITS system. The quantity of water that can be recovered from an ITS system for cooling intake-air is also found to be significant.

Dry Cooling Systems Efficiency Improvement

This project focused on the development of a high thermal conductivity foam to be used as the heat transfer medium in an ACC for power plants equipped with a dry cooling system. A Chevron fin design that was fabricated and tested exceeded the performance of the optimized commercial aluminum fin design by approximately 16 percent. The design for the pilot-scale heat exchanger has been completed where the design allows for both the conventional aluminum fin tube and carbon foam coils to be installed between the manifolds.

Air2Air Condensing Technology for Evaporative Water Loss Reduction [FY 2007]

A test cooling tower cell using the experimental Air2Air technology has been constructed on its host power plant site—the San Juan Generating Station in Farmington, NM. The cell will be tested for the next year to evaluate its performance in all weather conditions. Performance under freezing conditions, which is of particular concern due to potential damage to the cell will also be determined.

4.5. ADVANCED WATER TREATMENT AND DETECTION TECHNOLOGY

Specific research areas in Advanced Water Treatment and Detection Technology are cooling water intake system efficiency improvement through control of zebra mussel fouling, passive waste water treatment systems (constructed wetlands) for power plant wastewater, non-traditional waters for reuse in power generation and mine lands reclamation, and advanced clay-based adsorbent for power plant waste water treatment. Table 8 provides additional information on participating researchers and a brief description of their projects in this category.

Table 8. Participating Research Organizations and Project Descriptions	
Researcher	Project Description
New York State Education Department (New York State Museum) [FY 2007]	Kill zebra mussels using a particular strain of a naturally occurring bacterium, <i>Pseudomonas fluorescens</i> .
Tennessee Valley Authority, EPRI [FY 2007]	Use a passive treatment technology to remove trace levels of Arsenic, Selenium, mercury, ammonium, and nitrate from coal-fired power plants.
EPRI, West Virginia University [FY 2007]	Demonstrate the efficacy of reclaiming abandoned mine land (AML) in the Appalachian mining region.
University of Southern California	Use magnesium-aluminum carbonate layered double hydroxides to treat and reuse power plant effluents in batch experiments.
Clemson University	Construct a pilot-scale wetland treatment system for coal-fired power plants equipped with FGD controls.
Clemson University [FY 2007]	Construction of a pilot-scale wetland treatment system to control targeted constituents in non-traditional waters for reuse in thermoelectric power plants.

Cooling Water Intake System Efficiency Improvement through Control of Zebra Mussel Fouling [FY 2007]

Experiments conducted at the New York State Museum’s Field Research Laboratory on the intake water treatment system for Rochester Gas and Electric Corporation’s (RG&E) Russell Station succeeded in achieving some 88 percent reduction in the cost of preparing the fermentation medium needed to produce high yields of toxic bacterium cells, called *Pseudomonas fluorescens*. When a zebra mussel ingests artificially high amounts of this bacterium, the biotoxin within these bacterial cells destroys the mussel’s digestive system. Results obtained so far indicate that, in zebra mussel populations held in small pipes, 70 to 100 percent mortality can be routinely achieved. This bacterial approach to zebra mussel control has now become more economically competitive with the cost of biocides currently used by power plants.

Passive Waste Water Treatment Systems (Constructed Wetlands) [FY 2007]

- **Mine Lands Reclamation**

A limestone channel has been successfully constructed and is being used for water treatment from acid mine drainage that flows into Sovern Run (a tributary of Big Sandy Creek) in West Virginia. The pH of the water entering the receiving stream improved

significantly by channeling the water through the treatment system. Water quality was measured and conventional economic principles were used to develop the costs and environmental benefits of the remedial treatments. Potential environmental credits considered included water quality credits due to decreased acid mine drainage and other benefits resulting from the soil amendment, as well as potential credits at other sites for CO₂ sequestration.

- **Power Plant Wastewater**

The constructed wetland treatment system successfully decreased aqueous concentrations of arsenic (As), mercury (Hg), and selenium (Se) for the majority of the tested wastewaters. Mercury removal was consistently greater than 90 percent for three of the simulated FGD wastewaters and ranged from 64 to 97 percent for all FGD wastewaters except for the high ionic strength FGD wastewater where the mercury was already below the National Pollutant Discharge Elimination System (NPDES) permit level of 0.001 mg/L. Selenium removal rates were relatively stable with a range of 84 to 90 percent. Arsenic removal varied somewhat, but with higher removal rates (~70 percent) occurring with the high ionic strength FGD wastewater. Tests conducted using sequential extraction procedures indicated that most of the As, Hg, and Se is bound with the residue phases within the sediment, and the dissolution of these elements is unlikely to occur under typical environmental conditions within the treatment system. Furthermore, toxicity experiments demonstrated a significant increase in survival, growth, and reproduction for organisms exposed to samples of the simulated FGD wastewater outflow versus inflow. Satisfactory chloride levels (~4000mg/L) were achieved by dilution with moderately hard water.

- **Non-Traditional Waters for Reuse in Power Generation.**

The pilot-scale constructed wetland treatment system (CWTS) to control targeted constituents in non-traditional waters (such as FGD waters and produced waters) for reuse in thermoelectric power plants showed that these systems decreased constituents of concern in FGD water and produced water. A conceptual depiction of a CWTS is shown in Figure 5.

- *FGD water:* The CWTS decreased aqueous concentrations as follows: 40.1 to 77.7 percent for As, 77.6 to 97.8 percent for Hg, 43.9 to 88.8 percent for nitrogen, and no removal to 84.6 percent for Se. Reuse of FGD waters will be assessed in future testing, but based on total dissolved solids, co-management techniques will need to be implemented for discharge or reuse.
- *Produced water:* The CWTS decreased aqueous concentrations as follows: 38.4 to 99.6 percent for cadmium, 90.6 to 99.8 percent for copper, 93.1 to 99.3 percent for lead, and 40.0 to 99.8 percent for zinc. Reuse of these waters will likely depend on chloride concentration of the outflow, but with use of reverse osmosis technology, chloride concentrations may be decreased sufficiently for reuse as service water.



Figure 5. Conceptual Depiction of a CWTS

Advanced Clay-Based Adsorbent for Power Plant Waste Water Treatment

A University of Southern California study on the utilization of novel anionic clay sorbents (calcined and uncalcined layered double hydroxides [LDH]) for treating and reusing power plant effluents showed that the calcined materials exhibited higher adsorption capacity and efficiency than the uncalcined sorbent. This was attributed to the higher surface areas of the former materials. Furthermore, when calcined sorbents are in contact with anion-containing waters, they rapidly re-hydrate and adsorb the anions in the process reconstructing their original structure. In Phase 2, researchers have developed a film surface-diffusion model to describe the packed-bed column behavior. Preliminary investigations indicate that the model developed is successful in describing As (V) adsorption.

4.6. SYSTEMS ANALYSIS AND POLICY SUPPORT

Water Use Projection Study [FY 2007]

NETL estimated future freshwater withdrawal and consumption requirements for the U.S. thermoelectric generation sector for five cases:

- Case 1 – Additions and retirements are proportional to current water source and type of cooling system.
- Case 2 – All additions use freshwater and wet recirculating cooling, while retirements are proportional to current water source and cooling system.
- Case 3 – 90 percent of additions use freshwater and wet recirculating cooling, and 10 percent of additions use saline water and once-through cooling, while retirements are proportional to current water source and cooling system.

- Case 4 – 25 percent of additions use dry cooling and 75 percent of additions use freshwater and wet recirculating cooling. Retirements are proportional to current water source and cooling system.
- Case 5 – Additions use freshwater and wet recirculating cooling, while retirements are proportional to current water source and cooling system. Five percent of existing freshwater once-through cooling capacity is retrofitted with wet recirculating cooling every five years starting in 2010. The following summary results in Table 9 were found on a national basis.

Table 9. Thermoelectric Water Impacts, National Results							
		Freshwater withdrawal or consumption (BGD)					
		2005	2010	2015	2020	2025	2030
Case 1	Withdrawal	149.2	152.7	145.6	147.6	148.8	148.4
	Consumption	6.2	6.6	6.8	7.3	7.6	7.9
Case 2	Withdrawal	149.2	149.4	141.0	138.6	138.0	136.3
	Consumption	6.2	6.7	6.9	7.5	7.9	8.2
Case 3	Withdrawal	149.2	149.4	140.9	138.5	137.9	136.1
	Consumption	6.2	6.6	6.9	7.4	7.8	8.1
Case 4	Withdrawal	149.2	149.3	140.8	138.3	134.6	135.4
	Consumption	6.2	6.6	6.8	7.3	7.4	7.5
Case 5	Withdrawal	149.2	137.7	122.7	114.2	109.4	103.7
	Consumption	6.2	6.9	7.4	8.2	8.7	9.2

For all cases, withdrawal is expected to decline, and consumption is expected to increase. These results are consistent with current and anticipated regulations and industry practice, which favor the use of freshwater recirculating cooling systems that have lower withdrawal requirements, but higher consumption requirements, than once-through cooling systems. Converting a significant share of existing once-through freshwater power plants to recirculating freshwater plants significantly reduces water withdrawal but significantly increases water consumption. Case 4 indicates that dry cooling could have a significant impact on water consumption; compared with Cases 1-3, which have an average consumption of 8.1 BGD, Case 4 results in a 7 percent decline, equivalent to more than 200 billion gallons per year. Case 5 provides the most extreme water consumption impacts, with significantly reduced withdrawal and increased consumption compared with the other cases.

4.7. IN-HOUSE WATERSHED SCIENCE & TECHNOLOGY R&D

Specific research areas under the In-House Watershed Science and Technology R&D program are Geophysical Investigations, Novel Biosensors for the Detection of Environmental Contaminants, Bioremediation, and Mine Water.

Geophysical Investigations

Successful activities include use of helicopter electromagnetic and night-time thermal infrared surveys to:

- Detect and map contaminated groundwater at abandoned coal mines in north-central Pennsylvania and at an abandoned mercury mine in California
- Identify potentially hazardous conditions (unconsolidated slurry pockets, high phreatic zones, and shallow underground mines) at 14 coal waste impoundments in southern West Virginia with a moderate to high hazard potential
- Determine the best management strategy for water co-produced with coalbed natural gas in the Powder River Basin of Wyoming
- Develop airborne and ground-based well finding strategies for surveying both large, open areas and small, highly developed areas
- Develop mobile platforms for ground surveys in areas where airborne surveys are not possible or practical

5. NO_x CONTROL TECHNOLOGIES

5.1. SUBPROGRAM SUMMARY

The DOE NO_x control program seeks to reduce NO_x emissions per megawatt while simultaneously lowering costs beyond what can be achieved with current low-NO_x burners (LNB) and SCR. The current short-term goal of the research is to develop advanced in-furnace technologies for coal-fired power plants capable of controlling NO_x emissions to a level of 0.15 lb/MMBtu by 2007 and 0.10 lb/MMBtu by 2010, while achieving a levelized cost savings of at least 25 percent compared with state-of-the-art SCR technology. The program's long-term goal is to further develop a combination of advanced in-furnace and SCR control technologies to achieve a NO_x emission rate of 0.01 lb/MMBtu by 2020.

NETL has been at the forefront of conducting advanced NO_x control technology R&D for coal-fired power plants. The success of achieving the required Title IV acid rain program NO_x reductions can be attributed largely to the adoption of LNB technology by the utility industry. The LNBs that are currently installed in 75 percent of the nation's coal-fired power plants are a direct result of the DOE Clean Coal Technology Program government–industry partnerships.

The continuing ratcheting down of NO_x emissions by new regulations will require some power plant emission rates to be reduced well beyond 0.15 lb/MMBtu. To meet these requirements, power producers will need to retrofit existing boilers with additional NO_x control technologies, some of which will adversely impact plant efficiency and performance. The new NO_x control requirements demand an increase in R&D, capital, and operating expenditures from power plants to implement and they come at an inopportune time for an industry that has been adversely impacted financially by deregulation and its associated capital market pressures, aging facilities,

and homeland security concerns, in addition to other ever-expanding environmental control requirements.

In response to this challenge, NETL is partnering with industry and academia through the IEP Program to conduct advanced NO_x control technology R&D. The specific performance target is to develop combustion control technologies for existing plants with a NO_x emission rate of 0.15 lb/MMBtu by 2006 and 0.10 lb/MMBtu by 2010, while achieving a levelized cost savings of at least 25 percent compared with state-of-the-art SCR control technology. A long-range goal is to further develop a combination of advanced combustion and SCR control technologies to achieve a NO_x emission rate of 0.01 lb/MMBtu by 2020. However, in a cap-and-trade allowance-based regulatory program, it is realized that low-cost NO_x control technologies that do not achieve the target emission rates can still have a prominent role as a compliance strategy. Further, the technologies under development are intended to have negligible impact on BOP issues, to be applicable to a wide range of boiler types and configurations, and to be capable of maintaining performance over a wide range of feed coals and operating conditions. The research portfolio includes advanced combustion controls, advanced flue gas treatment, and integrated control systems. The following sections include brief summaries of several current NETL advanced NO_x control technology R&D projects.

5.2. ADVANCED IN-FURNACE TECHNOLOGIES FOR EXISTING AND NEW PLANTS

Ultra-Low NO_x Burners for Tangentially Fired Boilers

Alstom Power Inc., completed a pilot-scale study to develop retrofit NO_x control technology for tangentially fired boilers where its TFS 2000™ low-NO_x firing system was refined to further decrease NO_x emissions and improve related combustion performance. Among the refinements evaluated were finer coal grinding, oxidative pyrolysis burners, windbox auxiliary air optimization, and various burner zone firing arrangements in concert with overfire air. Other technologies, such as an advanced boiler control system, coal and airflow balancing, and a carbon burn out combustor were also evaluated. The pilot-scale modified TFS 2000 system was able to achieve NO_x emissions of less than 0.1 lb/MMBtu while firing PRB coal and less than 0.15 lb/MMBtu while firing highly volatile bituminous coal.

Ultra-Low NO_x Burners for Wall-Fired Boilers

McDermott Technology, Inc., Babcock & Wilcox Company, and Fuel Tech teamed to conduct pilot-scale testing of an integrated NO_x control solution for wall-fired boilers. The system was comprised of B&W's DRB-4Z™ LNB technology and Fuel Tech's NO_xOUT®, a urea-based selective non-catalytic reduction (SNCR) technology. The ULNB-SNCR combination achieved a controlled NO_x emission rate of approximately 0.23 lb/MMBtu with bituminous coal and 0.11 lb/MMBtu with subbituminous coal.

Rich Reagent Injection for Wall and Cyclone-Fired Boilers

Reaction Engineering International optimized the EPRI Rich Reagent Injection (RRI) process for NO_x reduction on cyclone burners. RRI uses a nitrogen-containing additive, such as ammonia or urea, to non-catalytically reduce NO_x in the lower furnace. Full-scale field testing of RRI was conducted at Conectiv's 138 MW B.L. England Unit 1 and AmerenUE's 500 MW Sioux Unit 1.

This project also included testing of optional SNCR. The RRI-SNCR combination achieved a controlled NO_x emission rate of approximately 0.25 lb/MMBtu with bituminous coal.

Oxygen-Enhanced Combustion for Pulverized and Cyclone-Fired Boilers

Praxair, Inc. and its partners developed a novel oxygen-enhanced combustion (OEC) technology that can reduce NO_x emissions from pulverized coal (PC)-fired boilers, while improving combustion characteristics such as LOI. This novel technology replaces a small fraction of the combustion air with oxygen. Praxair is also developing an oxygen transport membrane process that uses pressurized ceramic membranes for separation of oxygen from air. Pilot-scale testing conducted using a commercially available wall-fired burner with OEC demonstrated less than 0.15 lb/MMBtu NO_x emissions could be achieved while firing Illinois No. 6 bituminous coal. In November 2005, Praxair's OEC NO_x control system was recognized as one of five finalists for *Chemical Engineering* magazine's prestigious Kirkpatrick Award for Chemical Engineering Achievement.

Enhanced Combustion Low-NO_x Burner for Tangentially-Fired Boilers [FY 2007]

Alstom Power, Inc. is developing an enhanced combustion, low-NO_x burner for tangentially-fired boilers. The objective is to optimize combustion via control of near-burner time, temperature, turbulence, and stoichiometry. Candidate low-NO_x burner components being tested include enhanced coal nozzle tips and internal and external air and fuel separators. These components are being integrated into Alstom's latest generation of the TFS 2000 firing system. The enhanced low-NO_x burner is designed to achieve an emission rate of less than 0.15 lb/MMBtu and have minimal BOP impacts while burning high-volatile bituminous coal. The project includes computational fluid dynamics (CFD) modeling and large pilot-scale testing (approximately 50 MMBtu/hr) to provide information for designing a full-scale version of the enhanced low-NO_x burner.

Advanced In-Furnace NO_x Control for Wall- and Cyclone-Fired Boilers [FY 2007]

Babcock & Wilcox Company is developing and demonstrating an advanced NO_x control technology capable of achieving an emission rate of 0.10 lb/MMBtu while burning high-volatile bituminous coal for both wall and cyclone-fired boilers. The technology is based on a "layered" strategy that combines deep air staging using overfire air (OFA), continuous corrosion monitoring, advanced combustion control enhancements, and a proprietary combustion technique using oxygen injection. The stoichiometric ratio (SR) in the main combustion zone is varied from 0.8 to 1.1. The re-burn zone features oxygen-enhanced combustion of the re-burn fuel and flue gas recirculation (FGR), at an SR of less than 1. The burnout zone utilizes OFA to achieve complete combustion, at an SR greater than 1.

Full-Scale Field Testing of ALTA NO_x Control for Cyclone-Fired Boilers [FY 2007]

Reaction Engineering International (REI) conducted CFD modeling and full-scale field testing to evaluate a NO_x control technology known as Advanced Layered Technology Application (ALTA). ALTA combines deep staging with OFA, rich reagent injection (RRI), and selective

non-catalytic reduction (SNCR) to achieve NO_x emissions near 0.10 lb/MMBtu in cyclone boilers. Developed by REI and the Electric Power Research Institute, RRI uses a nitrogen-containing additive, such as ammonia or urea, to non-catalytically reduce NO_x in the lower furnace. REI conducted field testing in May and June of 2005 at AmerenUE's Sioux Station Unit 1, a 500 MW cyclone boiler unit that typically burns an 80/20 blend of PRB subbituminous coal and Illinois No. 6 bituminous coal. Parametric testing was also conducted with 60/40 and 0/100 blends. The testing also evaluated process impacts on BOP issues such as the amount of unburned carbon in the ash, slag tapping, waterwall corrosion, ammonia slip, and heat distribution.

Pilot-Scale Testing of ALTA NO_x Control for Wall-Fired Boilers [FY 2007]

REI is also developing and verifying performance of the ALTA NO_x control technology for wall-fired boiler applications to achieve an emission rate of less than 0.15 lb/MMBtu. The burners are being designed for complete near-burner combustion, rather than traditional staged combustion. Near-burner design provides greater homogeneity of the combustion products in the boiler. Not only does this create ideal conditions for combustion-related NO_x control, it also results in a stoichiometry and temperature distribution above the burners that is ideal for the chemistry involved in RRI. REI is conducting CFD modeling and pilot-scale testing to optimize the near-burner combustion system and reagent injection. The pilot-scale testing is being conducted on a 5 million Btu/hr coal combustion furnace operated by the University of Utah. REI will be conducting a second set of CFD modeling studies based on initial pilot-scale combustion results to refine the process design. The final task of the project will involve CFD modeling of a full-scale boiler to evaluate the impact of burner modifications combined with deeper staging and RRI on NO_x emissions, unburned carbon, waterwall corrosion, and boiler heat balance.

5.3. ADVANCED POST-COMBUSTION NO_x CONTROL TECHNOLOGIES

Real-Time Catalyst Deactivation Measurements in Full-Scale SCR Systems [FY 2007]

Fossil Energy Research Corporation (FERCo) has developed an *in situ* catalyst deactivation measurement device for optimized catalyst management. The device collects real-time SCR performance data by continuously measuring catalyst activity. As the data are collected, they are analyzed by an existing catalyst management software program, providing information on boiler operating conditions that negatively impact catalyst activity. This information can then be used to optimize boiler operation with respect to the catalyst deactivation rate and the catalyst replacement schedule.

Commercial-Scale Implementations

The following R&D Projects in advanced NO_x control technology have been implemented commercially:

- In November 2005, Ameren announced its plans for evaluating a full-scale implementation of the Advanced Layered Technology Application, which is based on the

results of RRI and SNCR. This investigation is being conducted at the two 500 MW units at its Sioux Station.

- Nineteen commercial boilers firing PRB coal have achieved NO_x emissions below 0.15 lb/million BTU from the implementation of technologies developed in Alstom's TFS 2000™ low-NO_x firing system.
- Praxair's oxygen-based technology, installed on two coal-fired boilers at the P.H. Glatfelter pulp and paper mill in Spring Grove, PA showed that a cost savings of 40 to 50 percent may be achieved compared with SCR based on preliminary economic studies.
- The Knoxcheck Online Catalyst Activity Test System, developed with NETL funding, is now commercially available.

While SCR has been effective at removing NO_x from flue gas, a costly drawback is the need to either shut down the unit to sample and test catalyst activity, or to “guesstimate” its remaining activity. If the catalyst is replaced too early, the remaining life of the expensive catalyst is lost; if replaced too late, NO_x emissions from the power plant may become high enough to trigger an environmental audit.

The new Knoxcheck Online Catalyst Activity Test System, developed by Fossil Energy Research Corporation (FERCo), monitors catalyst activity in an SCR system without the need to shut down the unit to obtain catalyst samples. The new system is similar to non-invasive medical diagnostic techniques where the Knoxcheck system monitors the health of each SCR catalyst layer without taking the SCR system out of service. Technicians can measure catalyst activity during any unit load condition without disruption, allowing the power plant and its environmental controls to continue operating with minimum downtime. The system is now commercially available and is expected to save up to \$1.2 million for each avoided outage.

6. AIR QUALITY R&D

6.1. SUBPROGRAM SUMMARY

The Air Quality R&D subprogram is focused on bringing additional clarity to the scientific uncertainties associated with the emission, transport, transformation, and deposition of emissions from coal-based power systems. The goal is to provide information that can guide future policy decisions, by providing improved information on the specific needs for controls and by providing control technology options. Four major pathways, i.e., ambient monitoring and analysis, emissions characterization, predictive modeling and evaluation, and health effects are used to implement this subprogram. The ambient monitoring and modeling activity is designed to obtain a better understanding of the contribution of coal-fired power plants to concentration and composition of ambient particulate matter less than 2.5 micron in size (PM_{2.5}) and regional

haze. Emissions characterization is designed to obtain detailed information on fine particulate and mercury emissions from coal-based power systems, both in-stack and in the resultant plume.

6.2. AMBIENT MONITORING

The goal of ambient monitoring is to develop a reliable database on the composition and characteristics of ambient PM and gaseous species. The objectives from this include providing a set of high quality data on ambient air to the EPA and assessing trends in air quality relative to reductions in emissions.

Advanced Sampling and Analysis Methodologies

In a collaborative effort between ChemImage Biothreat, LLC and NETL, the Airborne Particulate Threat Assessment Project set out to acquire the ability to discern between chemical/biological threat agents and ambient background PM encountered in the environment. The project's initial conclusions are that dry electrostatic collection and deposition is the best approach for sampling ambient particulate matter for subsequent Raman spectroscopic detection. Also, from the team's evaluation of the deposition technologies, electrostatic aerosol collection of dry PM was selected as the preferred approach for its high collection efficiency, low overall cost, and compatibility with Raman identification.

Regional Based Air Quality Studies

NETL has engaged in regional based air quality studies as part of its ambient monitoring program, focusing on the upper Ohio River valley region. Three studies examine this region.

The Steubenville Comprehensive Air Monitoring Project (SCAMP) study has made strides in the analysis of water-soluble and total elements in fine PM. The objective of SCAMP was to measure the concentrations of PM_{2.5} and other potential air pollutants at ambient monitoring stations in and around Steubenville, OH, and relate them to the pollutant concentrations in air that is actually breathed by people living in the area. Steubenville was chosen by NETL for this study because of the ability to integrate its results with those of the Upper Ohio River Valley Project (UORVP) and also because Steubenville was one of the six cities where correlations between ambient PM_{2.5} mass and adverse health effects had been noted. These correlations had been cited by EPA as one of the primary justifications for its 1997 ambient PM_{2.5} standards. Complete characterization of the relationships between ambient PM_{2.5} and human exposure, including the chemical components of PM_{2.5} at various locations, provide a comprehensive database for use in subsequent epidemiological studies, long-range transport studies, and State Implementation Program development. CONSOL Energy was the primary performer of SCAMP and provided coordination and data integration between the various components of the study.

The data obtained as part of the UORVP study suggests that many regions within the UORV may be designated as non-attainment with respect to the annual PM_{2.5} standard. If this is realized, then the State Implementation Plans will likely mandate reducing air emissions of PM_{2.5} and/or its precursor gases from a large number of stationary, mobile, and area sources that are located within a large geographical area.

The Pittsburgh Air Quality Study (PAQS) is a comprehensive multidisciplinary set of projects in the Pittsburgh region that will address issues such as cost-effective PM control strategies, which are currently limited by the lack of understanding of PM health effects. PM health-effect data in turn are exacerbated by the lack of physiological data, the difficulty of establishing the PM source-receptor relationships, and the limitations of existing instrumentation for PM measurements. Recent accomplishments of the PAQS include the development of fingerprints for urban and rural road dust in Pittsburgh, the development of a fingerprint for vegetative detritus based on a composite sample of major tree types in the Pittsburgh region, and the analysis of vehicle emissions measured in tunnels to develop aggregate, fleet-average emission profiles for motor vehicles in the Pittsburgh area.

Web-Based PM Monitoring Database

Advanced Technology Systems, Inc., and its subcontractors (Ohio University and Texas A&M University-Kingsville) have developed a preliminary version of the public website which was used by NETL to advertise data availability and included a data retrieval tool to download the original data files associated with this project. The final objective is to develop a state-of-the-art, scalable and robust computer application for NETL to manage the extensive data sets resulting from the DOE-sponsored ambient air monitoring programs in the UORV region.

6.3. EMISSIONS CHARACTERIZATION

The goal of this section is to determine the chemical characteristics of emissions. The path forward to achieving this is to validate stack emissions data, provide emissions “signatures” to determine sources, and gather information on mercury transport and deposition for use in the development of mercury trading programs.

Particulate Matter Measurement Methods

UNDEERC has developed advanced sampling and analysis methodologies for PM that can be used for source apportionment and to assist in health studies. These techniques will be used to determine sources of PM_{2.5} in rural states such as North Dakota. Although there are a vast number of studies on PM, a significant portion, mainly polar PM constituents, still remains unidentified. Consequently, toxicological studies are limited when relating adverse health effects to known components. Using sub-critical water fractionation, which allows for extractions of neglected polar compounds, UNDEERC confirmed this hypothesis of the toxicological importance of typically neglected polar PM fractions. In addition, they showed that even samples of slightly different origin such as two diesel PM or ambient PM samples from Pittsburgh may have different toxicological impacts. Thus, the conditions at which PM was generated can significantly influence its toxicity.

Mercury Reactions in Power Plant Plumes

EPRI, in collaboration with Frontier Geosciences and UNDEERC determined that mercury can be measured in plumes by aircraft with reasonable accuracy and precision during their efforts to perform precise in-stack and in-plume sampling of mercury emitted from WeEnergy’s Pleasant Prairie plant near Kenosha, WI.

Impact of Low-NOx Burners on PM_{2.5} Emissions

The goal of this work is to develop a comprehensive, high-quality database characterizing PM_{2.5} emissions from utility plants firing high-sulfur coals. For all test conditions, the particulate removal efficiency of the ESP exceeded 99.3 percent and emissions were less than the New Source Performance Standard (NSPS) limits of ~48 mg/dscm. In general, the concentration of inorganic elements and trace species in the fly ash at the ESP inlet was dependent on the particle size fraction. The smallest particles tended to have higher concentrations of trace species than larger particles. The concentration of most elements by particle size range was independent of combustion condition and the concentration of soluble ions in the fly ash showed little change with combustion condition when evaluated on a carbon-free basis.

Pittsburgh Area Source Emissions Characterization Study

The emissions characterization study is being performed in conjunction with PAQS, a larger effort that includes ambient measurements and atmospheric modeling of the Pittsburgh region. The current performance of Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx) in the Eastern United States for the major aerosol components and PM_{2.5} during all seasons is encouraging. The improvement of the model performance during the last two years was mainly due to the comparison of the model predictions with the continuous measurements in the Pittsburgh Supersite. Major improvements have included the descriptions of ammonia emissions (Carnegie Mellon University inventory), night-time nitrate chemistry, elemental carbon (EC) emissions and their diurnal variation, and nitric acid dry removal.

6.4. PREDICTIVE MODELING AND EVALUATION

The goal of air quality predictive modeling and evaluation is to determine the likely emissions sources of species of concern. To do this, they must understand the impacts of different control strategies for use in public and regulatory deformations, along with the market-based compliance options.

Pittsburgh Air Quality Study

As stated above, the PAQS encompasses a wide range of work. Along with ambient monitoring, there is also a modeling and evaluation arm to the work. Some conclusions that have been reached trying to identify sources of PM_{2.5} include PSCF (potential source contribution function) and CPF conditional probability function) results for the positive matrix factorization-modeled factors in the study, and these sources can be grouped into three different categories:

- Regional sources: sulfate and selenium from coal-fired power plants in the Ohio River Valley
- Local sources: specialty steel, lead, and cadmium factors representing sources mostly within Allegheny County, PA
- Potentially regional or local sources: iron (Fe), manganese (Mn), and zinc (Zn) (from steel production industry); gallium-rich (unknown source)

PSCF and CPF results agree for the lead factor, the gallium-rich factor, and the specialty steel factor. PSCF results show the Ohio River Valley to the southwest as the source location for the sulfate, Se, Fe, Mn, and Zn factors, while CPF shows a more southeast most probable direction. Despite limitations in using 24-hour averaged ambient data, probable locations are determined for several of the modeled sources of PM_{2.5} by using PSCF and CPF

Ohio River Valley Study

Ohio University evaluated the impact of emissions from coal-fired power plants in the Ohio River Valley region as they relate to the transport and deposition of Hg, As, and associated fine PM. Meteorological simulations were completed for 2004 to support conducting seasonal-scale modeling simulations to identify sources contributing to the deposition of Hg, As, and PM_{2.5} in the Ohio River Valley region. Also, the development of web-based model interface technologies were initiated to enable industry and government agencies to evaluate pollutant source-receptor relationships and performance of emission reduction strategies.

Health Effects

The goal of this work is to improve the scientific data on health effects of plant emissions versus other sources. The Toxicological Evaluation of Realistic Emissions of Source Aerosols (THERESA) tri-city study was designed to investigate and clarify the impact of the sources and components of PM_{2.5} on human health via a set of realistic animal exposure experiments. Fieldwork was completed at the Southeast power plant, which burns eastern bituminous coal, with no changes in histology, bronchoalveolar lavage fluid, or blood cytology evident. Stage II assessment suggest no apparent effect of any of the scenarios on heart rate or on several measures of heart rate variability. However, one scenario did result in an increase in cardiac arrhythmias in exposed animals compared with control animals.