ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)–U.S. DEPARTMENT OF ENERGY (DOE) JOINT PROGRAM ON RESEARCH AND DEVELOPMENT FOR FOSSIL ENERGY-RELATED RESOURCES

Final Report

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ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)–U.S. DEPARTMENT OF ENERGY (DOE) JOINT PROGRAM ON RESEARCH AND DEVELOPMENT FOR FOSSIL ENERGY-RELATED RESOURCES

ABSTRACT

The EERC teamed with the DOE National Energy Technology Laboratory to conduct complementary research and development under the Joint Program on Research and Development for Fossil Energy-Related Resources (Cooperative Agreement No. DE-FC26-08NT43291). This 10-year program merged two previous 10-year agreements—DE-FC26-98FT40320 and DE-FC26-98FT40321—into a single follow-on agreement. The Fossil Energy cooperative agreement between DOE and the EERC was initiated in 1983 when the EERC was defederalized. This dynamic 35-year partnership has evolved to further research in areas that address DOE Office of Fossil Energy program goals while serving the missions and exploiting the strengths of both organizations through this agreement and a new 5-year Fossil Energy-Related Resources cooperative agreement established in 2015. As the 10-year program has ended, the purpose of this report is to summarize the activity and significant outcomes that were accomplished by the EERC.

This program is an excellent model for research, development, demonstration, and commercialization partnerships between government, industry, and the applied science and engineering communities to bring cutting-edge science closer to commercial application. The *overarching goal* was to support DOE Fossil Energy goals by advancing the scientific knowledge and technical development essential to ensuring future sustainable supplies of affordable energy and clean water, protecting and restoring the environment, and reducing dependence on foreign energy sources, thereby increasing U.S. energy security. The *strategic objective* was to advance continued use of domestic fossil fuels as a mainstay of U.S. energy production by making fossil energy systems nonpolluting and more efficient, capturing and sequestering greenhouse gases, and integrating the use of fossil and renewable energy sources into the energy mix. The research achievements from this partnership have exceeded the goals and objectives by contributing substantially to the development of science-based energy and environmental policy, educational foundations for science and technology, and commercialization and international marketing of energy technologies. The program comprised 75 individual projects, which included basic/applied fossil energy research projects involving no cost share and development, demonstration, and commercialization projects (many derived from applied research projects) that included nonfederal cost share of approximately 40% (the contractually required minimum level of cumulative nonfederal cost share was 29%). In all, $32,798,698 of federal funding was leveraged with industry cash and in-kind cost share of $21,697,129 from 80 nonfederal partners for a total of $54,495,827 of funded research that 1) advanced the development of unconventional tight oil resources in the Bakken Formation; 2) demonstrated the application of CO_2 Storage and EOR in tight oil formations; 3) developed advanced carbon capture technology; 4) addressed key application and infrastructure concerns for commercial deployment of CO_2; 5) demonstrated innovative, integrated water management strategies for energy development projects; 6) developed novel pollution control technologies for mercury and hazardous air pollutants; and 7) performed world-class outreach and dissemination of research results to industry partners and other stakeholders. These outcomes speak to the valuable return on the substantial investment in this program.

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NOMENCLATURE

AC	activated carbon
ACC	air-cooled condenser
$AFCO_2$	aqueous froth CO_2
acfm	actual cubic feet per minute
AFR	Advanced Fuel Research, Inc.
AFRL	Air Force Research Laboratory
AGD	Average Global Database
AH	air heater
Al	aluminum
API	American Petroleum Institute
AQ	Air Quality
ARPA-E	Advanced Research Projects Agency-Energy
As	arsenic
ASTM	ASTM (formerly American Society for Testing and Materials) International
Ba	barium
BAC	brominated activated carbon
Bbbl	billion barrel
bbl	barrel
BDSS	Bakken Decision Support System
Be	beryllium
BNDL	beneficiated North Dakota lignite
BP	budget period
Btu	British thermal unit
BYU	Brigham Young University
°C	degree Celsius
Ca	calcium
CAA	Clean Air Act
$CaCO_3$	calcium carbonate
CaO	calcium oxide
$Ca(OH)_2$	calcium hydroxide
$CaSO_4$	calcium sulfate
CATM	Center for Air Toxic Metals®
CBM	coalbed methane
CC	Carbon Capture program area
CCAT	Connecticut Center for Advanced Technology
CCB	coal combustion by-product
CCC	Canadian Carbon Converters, Inc.
CCP	coal combustion product
CCS	carbon capture and storage
Cd	cadmium
CEM	continuous emission monitor

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NOMENCLATURE (continued)

CES	Cooper Environmental Services
CFBC	circulating fluidized-bed combustion
CH_4	methane
Cl	chlorine
CLR	Continental Resources, Inc.
cm^2	square centimeter
CMG	Computer Modelling Group Ltd.
CMM	continuous mercury monitor
CNG	compressed natural gas
Co	cobalt
CO	carbon monoxide
CO_2	carbon dioxide
COC	contaminants of concern
COS	carbonyl sulfide
Cr	chromium
CRD	Cooperative Research and Development program area
CRDP	Cooperative Research and Development Partnerships program area
CS	Carbon Sequestration/Storage program area
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSLF	Carbon Sequestration Leadership Forum
CTF	combustion test facility
Cu	copper
$Cu(NO_3)_2$	copper(II) nitrate
$Cu(OH)_2$	copper(II) hydroxide
CVAA	cold-vapor atomic absorption
DAC	data acquisition and control
DCL	direct coal liquefaction
DDC	desiccant dry cooling
DEA	diethanolamine
dNm^3	dry normal cubic meter
DOE	U.S. Department of Energy
dscf	dry standard cubic foot
DSF	deep saline formation
DSS	decision support system
ECBM	enhanced coalbed methane
ECO-AFS	ECO-Alternative Fuel Systems
EERC	Energy & Environmental Research Center
EFG	entrained-flow gasifier
EGU	electric generating unit
EIA	U.S. Energy Information Administration
EOR	enhanced oil recovery

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NOMENCLATURE (continued)

EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
EUEC	Energy, Utility & Environment Conference
F	farad
°F	degree Fahrenheit
FDU	feasibility demonstration unit
Fe	iron
Fe^{2+}	ferrous iron
Fe^{3+}	ferric iron
$Fe(NO_3)_3$	iron(III) nitrate
Fe_2O_3	iron(III) oxide
FGD	flue gas desulfurization
FT	Fischer–Tropsch
ft^3	cubic foot
FTIR	Fourier transform infrared
g	gram
gal	gallon
GHG	greenhouse gas
GHGT	Greenhouse Gas Technologies (International Conference on)
GIS	geographic information system
GPE	GreatPoint Energy
gpm	gram per minute
GRE	Great River Energy
Gt	gigaton
GWP	global warming potential
HAP	hazardous air pollutant
HBr	hydrogen bromide
HCl	hydrochloric acid
Hg	mercury
Hg^0	elemental mercury
Hg^{2+}	inorganic mercury
$HgCl_2$	mercuric chloride
HHV	higher heating value
H_2O_2	hydrogen peroxide
HPFBG	high-pressure fluidized-bed gasifier
hr	hour
H_2S	hydrogen sulfide
H_2SeO_3	selenous acid
H_2SO_4	sulfuric acid
HTD	hydrothermal dewatering

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NOMENCLATURE (continued)

HWD	hot-water drying
ICCI	Illinois Clean Coal Institute
ICL	indirect coal liquefaction
ICR	information collection request
i.d.	inside diameter
IEA	International Energy Agency
IEAGHG	IEA Greenhouse Gas R&D Programme
IECM	Integrated Environmental Control Model
IEP	Innovations for Existing Plants program area
IGCC	integrated gasification combined cycle
in.	inch
K	potassium
KBR	Kellog, Brown and Root, Inc.
kcal	kilocalorie
KCl	potassium chloride
KCRC	Korea Carbon Capture and Sequestration R&D Center
kg	kilogram
kgal	kilogallon
kJ	kilojoule
KOH	potassium hydroxide
kPa	kilopascal
kW	kilowatt
kWh	kilowatt hour
L	liter
lb	pound
LDDS	liquid dessicant and dehumidification system
LEC	Lignite Energy Council
L/G	liquid/gas
LRC	low-rank coal
m	meter
M	molar
m^2	square meter
m^3	cubic meter
M26	Method 26 (EPA)
M26a	Method 26a (EPA)
M29	Method 29 (EPA)
M30B	Method 30B (EPA)
mA	milliampere
MACT	maximum achievable control technology
Macf	thousand actual cubic feet
MATS	Mercury and Air Toxics Standards

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NOMENCLATURE (continued)

Mcf	million cubic feet
MDEA	methyldiethanolamine
MEA	monoethanolamine
MeHg	methylmercury
MEST	multielement sorbent trap
MEST-H	multielement sorbent trap method for HCl
MEST-M	multielement sorbent trap method for metals
mg	milligram
Mg	magnesium
$MgCO_3$	magnesium carbonate
MGD	million gallon per day
MgO	magnesium oxide
MJ	megajoule
mL	milliliter
MM29	modified Method 29 (EPA)
MMBtu	million British thermal unit
MMP	minimum miscibility pressure
Mn	manganese
mol	mole
mol%	mole percent
MPa	megapascal
Mt	million ton
MVA	monitoring, verification, and accounting
MW_e	megawatt electric
N_2	nitrogen gas
Na	sodium
Na_2O	sodium oxide
NAPL	nonaqueous-phase liquid
NCHT	National Center for Hydrogen Technology
NDDH	North Dakota Department of Health
NDIC	North Dakota Industrial Commission
NDPC	North Dakota Petroleum Council
NESHAPs	National Emissions Standards for Hazardous Air Pollutants
NETL	National Energy Technology Laboratory
NG&O	Natural Gas and Oil program area
NGCC	natural gas combined cycle
NGL	natural gas liquid
NGPWC®	Northern Great Plains Water Consortium
NGV	natural gas vehicle
NH_3	ammonia
Ni	nickel

Continued . . .

NOMENCLATURE (continued)

NIST	National Institute of Standards and Technology
nm	nanometer
Nm^3	normal cubic meter
NO	nitric oxide
NO_2	nitrogen oxide
NO_x	nitrogen oxides
NPPD	Nebraska Public Power District
NSG	Neumann Systems Group
O_2	oxygen
OFA	overfire air
OMB	Office of Management and Budget
OPEC	Organization of the Petroleum Exporting Countries
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCA	principal component analysis
PCO_2C	Partnership for CO_2 Capture
PM	particulate matter
PPB	Prairie Public Broadcasting
ppm	parts per million
ppmv	parts per million volume
PPR	Prairie Pothole Region
PRB	Powder River Basin
PSA	pressure swing adsorption
psi	pounds per square inch
psig	pounds per square inch gauge
PTC	particulate test combustor
PTFE	polytetrafluoroethylene
PWR	Pratt & Whitney Rocketdyne
PZ	piperazine
QA/QC q	uality assurance/quality control
QEMSCAN®	Quantitative Elemental Mapping by Scanning Electron Microscopy
RA	relative accuracy
RAC	Research Advisory Council
RCRA	Resource Conservation and Recovery Act
R&D	research and development
RD	relative difference
s	second
S	sulfur
SACA	Standard Alcohol Company of America
Sb	antimony
scfm	standard cubic foot per minute

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NOMENCLATURE (continued)

S/cm	siemens per centimeter
SCR	selective catalytic reduction
SDA	spray dryer absorber
Se	selenium
SEA	sorbent enhancement additive
SEM	scanning electron microscopy
SeO_2	selenium dioxide
Si	silicon
SIPC	Southern Illinois Power Company
SMR	steam methane reforming
SNESS	Strategic National Energy Security Solutions program area
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_x	sulfur oxides
SOC	soot (or black) organic carbon
SPME	solid-phase microextraction
SRM	standard reference material
SRS	strip ray scanning
SS	stainless steel
ST	sorbent trap
STEPCON®	stepped control
SVE	soil vapor extraction
TAQA	TAQA North USA
TDS	total dissolved solids
Ti	titanium
TiO_2	titanium dioxide
TOC	total organic carbon
ton	short ton
tonne	metric ton
tpd	tons per day
TRDU	transport reactor development unit
TRIG™	transport reactor integrated gasification
TSA	temperature swing adsorption
µm	micrometer
UND	University of North Dakota
USGS	U.S. Geological Survey
UV	ultraviolet
µW	microwatt
V	vanadium
V	volt
vol%	volume percent

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NOMENCLATURE (continued)

W	watt
WEST	Water and Energy Sustainability and Technology (Program)
WFGD	wet flue gas desulfurization
WGS	water–gas shift
wt%	weight percent
WTI	West Texas Intermediate
XRD	x-ray diffraction
Zn	zinc

ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)–U.S. DEPARTMENT OF ENERGY (DOE) JOINT PROGRAM ON RESEARCH AND DEVELOPMENT FOR FOSSIL ENERGY-RELATED RESOURCES

EXECUTIVE SUMMARY

The University of North Dakota (UND) Energy & Environmental Research Center (EERC) teamed with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) to conduct complementary research and development under the Joint Program on Research and Development for Fossil Energy-Related Resources (Cooperative Agreement No. DE-FC26-08NT43291). This 10-year program (May 1, 2008 – May 31, 2018) merged two previous 10-year agreements—DE-FC26-98FT40320 (Base Agreement) and DE-FC26-98FT40321 (Jointly Sponsored Research Program)—into a single follow-on agreement. The Fossil Energy cooperative agreement between DOE and the EERC was initiated in 1983 when the EERC—then a DOE federal energy technology center—was defederalized and became part of UND. This dynamic 35-year partnership has provided critical and strategic technology development to address research needs in the DOE Office of Fossil Energy research programs while serving the missions and exploiting the strengths of both organizations through this agreement and a new 5-year Fossil Energy-Related Resources cooperative agreement established in 2015 (No. DE-FE0024233). As the 10-year program has ended, the purpose of this report is to summarize the activity and significant outcomes that were accomplished by the EERC.

The Joint Program on Research and Development for Fossil Energy-Related Resources is an excellent model for research, development, demonstration, and commercialization partnerships between government, industry, and the applied science and engineering communities to bring cutting-edge science closer to commercial application. The *overarching goal* of the program was to support DOE Fossil Energy goals by advancing the scientific knowledge and technical development essential to ensuring future sustainable supplies of affordable energy and clean water, protecting and restoring the environment, and reducing dependence on foreign energy sources, thereby increasing U.S. energy security. The *strategic objective* was to advance continued use of domestic fossil fuels as a mainstay of U.S. energy production by making fossil energy systems nonpolluting and more efficient, capturing and sequestering greenhouse gases, and integrating the use of fossil and renewable energy sources into the energy mix. The research achievements from this partnership have exceeded these goals and objectives by contributing substantially to the development of science-based energy and environmental policy, educational foundations for science and technology, and commercialization and international marketing of energy technologies.

This program included basic/applied fossil energy research projects that spanned low, middle, and high technology readiness levels. Overall cost share to projects in this program has approached 40%, significantly exceeding the 29% overall requirement. This level of cost share indicates strong involvement and commitment from industry partners. Projects were cost-shared in the form of cash and/or cash-equivalent that met all criteria required by Office of Management and Budget Circular A-110. Nonfederal partners in this program included oil and gas industry stakeholders, energy companies, utilities, industry service organizations, state agencies,

universities and other research entities, regional and local governments, technology vendors, and other private sector companies from the United States and across the world.

Projects complementary to DOE's program were chosen to bridge the gap between basic/applied research and technology development to accelerate the scale-up, demonstration, and commercialization of new and improved technologies. Approval of funding by DOE and nonfederal sponsors on a project-by-project basis ensured that the work performed had DOE program strategic significance and practical application in the private sector.

Continuation applications put forth research plans that addressed a variety of energy resources and related environmental issues, expressly recognizing the binding relationships that exist between recovery and use of resources, environmental impacts on ecosystems and watersheds, and the physical and economic security of the United States. The program provided flexibility to change the scope and content of research significantly from year to year to respond to DOE program priorities, evolving market needs, and available funding.

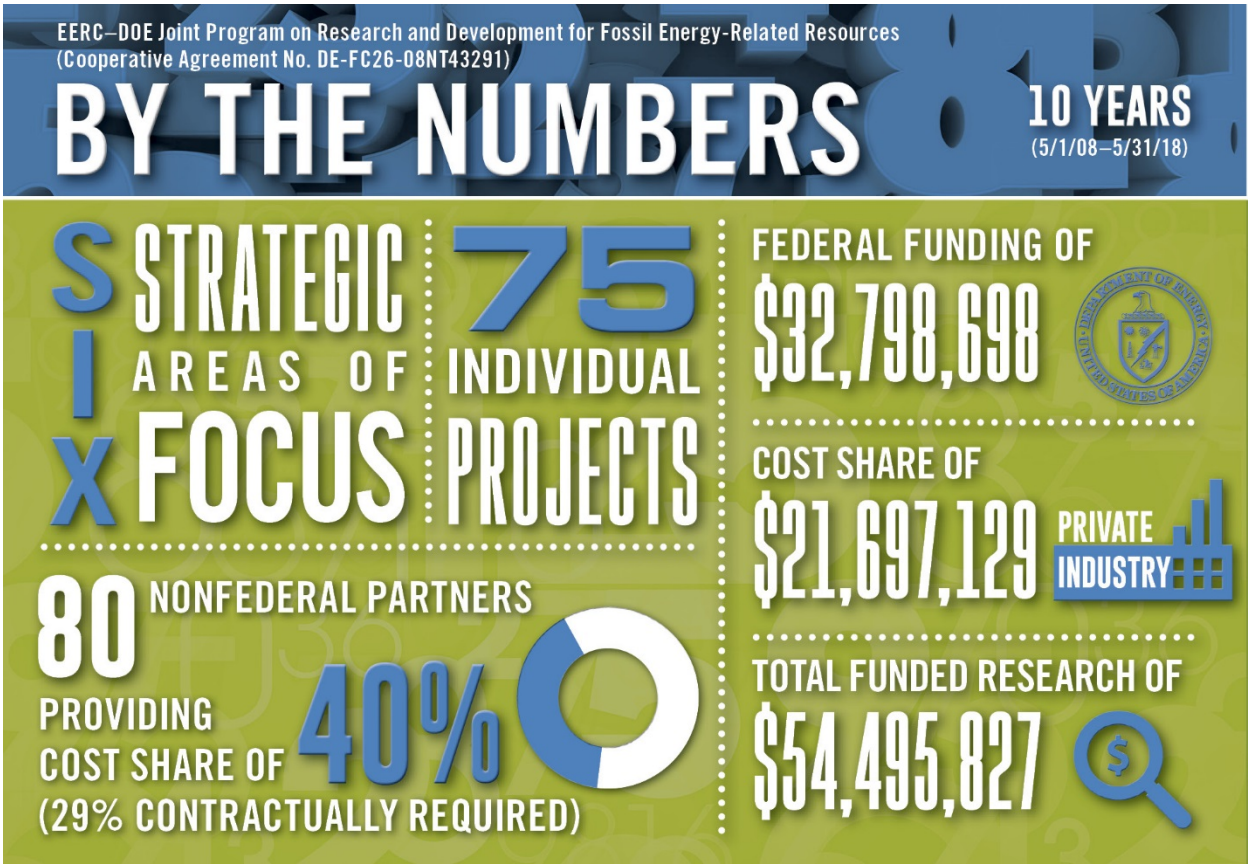
This program comprised seven tasks. Tasks 1.0–6.0 were based on six strategic areas of focus that contributed directly to and programmatically fit with DOE Fossil Energy goals and exploited the EERC's unique background and capabilities in low-rank coal (LRC) applications: 1) resource characterization and management, 2) climate change and CO_2 sequestration, 3) alternative fuels, 4) clean power systems, 5) water management and sustainability, and 6) strategic studies. Task 7.0 comprised the overall project management task. Individual projects under Tasks 1.0–6.0 were assigned subtask numbers and funded under one or more of seven program areas through one or a combination of eight federal funding sources. Program areas (with their associated funding sources) included 1) Cooperative Research and Development (CRD) (CRD), 2) CRD Partnerships (CRD), 3) Strategic National Energy Security Solutions (Congressional Directed Projects), 4) Innovations for Existing Plants (IEP) (IEP), 5) Natural Gas and Oil (Strategic Center for Natural Gas and Oil), 6) Carbon Sequestration/Storage (CS) (CS and Regional Carbon Sequestration Partnerships), and 7) Carbon Capture (CC) (CC and Postcombustion Capture).

By the numbers, this program comprised 75 individual projects that addressed six strategic areas of focus. In all, $32,798,698 of federal funding was leveraged with industry cash and in-kind cost share of $21,697,129 from 80 nonfederal partners for a total of $54,495,827 of funded research that 1) advanced the development of unconventional tight oil resources in the Bakken Formation; 2) demonstrated the application of CO_2 Storage and EOR in tight oil formations; 3) developed advanced carbon capture technology; 4) addressed key application and infrastructure concerns for commercial deployment of CO_2; 5) demonstrated innovative, integrated water management strategies for energy development projects; 6) developed novel pollution control technologies for mercury and hazardous air pollutants; and 7) performed world-class outreach and dissemination of research results to industry partners and other stakeholders. These outcomes speak to the valuable return on the substantial investment in this program.

ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)–U.S. DEPARTMENT OF ENERGY (DOE) JOINT PROGRAM ON RESEARCH AND DEVELOPMENT FOR FOSSIL ENERGY-RELATED RESOURCES

INTRODUCTION AND BACKGROUND

The University of North Dakota (UND) Energy & Environmental Research Center (EERC) teamed with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) to conduct complementary research and development (R&D) under the Joint Program on Research and Development for Fossil Energy-Related Resources (Cooperative Agreement No. DE-FC26-08NT43291). The quick facts below speak to the significance and impact of this highly successful partnership.



These numbers reflect the breadth of the program and the significant investment of DOE and nonfederal stakeholders in this partnership. The following page highlights just a portion of the valuable return on this significant investment.

Return on Investment

Advanced the Development of Unconventional Tight Oil Resources in the Bakken Formation

- Identified key attributes of successful Bakken wells and developed guidance tools for stakeholders, facilitating expansion of Bakken production from three North Dakota counties and one Montana county in 2009 to an essentially continuous resource that includes producing wells in eight North Dakota counties.
- Identified optimal proppant mixtures/loads that provide the best outcomes in hydraulic fracturing operations.
- Demonstrated and catalyzed prolific use of bifuel applications of wellhead gas in engines on drilling operations, reducing flaring and increasing economic efficiency.

Demonstrated the Application of CO_2 Storage and Enhanced Oil Recovery (EOR) in Tight Oil Formations

- Demonstrated the effectiveness of CO_2 to mobilize oil from the matrix of tight oil formations and that micro- to nanoscale fractures are primary pathways for CO_2 permeation and oil mobilization.
- Demonstrated that applying CO_2 EOR strategies that account for the unique properties of Bakken rocks can result in significant improvement in Bakken oil recovery factors.
- Verified that CO_2 can permeate the reservoir matrix and mobilize oil in the Bakken play.

Developed Advanced Carbon Capture Technology

- Demonstrated multiple solvents for several partners, leading to improved formulations, increased efficiency and, in some cases, full-scale demonstration.
- Demonstrated a partner's novel gas–liquid contactor system, leading to full-scale demonstration of the technology.
- Performed the first testing of a precombustion membrane on real syngas for a project partner.

Addressed Key Application and Infrastructure Concerns for Commercial Deployment of CO_2

- Developed CO_2 storage efficiency factors necessary for estimating CO_2 storage resource using the DOE method.
- Confirmed the applicability of current methods for estimating CO_2 storage resource.
- Supported the concept of using brine extraction to help reduce risk and monitoring costs by increasing CO_2 storage capacity, managing reservoir pressure, and controlling the CO_2 plume.
- Compiled lessons learned from real-world operating CO_2 transport and storage projects to better define practical operational considerations.

Demonstrated Innovative, Integrated Water Management Strategies for Energy Development Projects

- Demonstrated the feasibility of using alternative water supply sources to offset freshwater demand for energy production.
- Developed a geographic information system (GIS)-based decision support system that allows power generation facilities to address water supply issues when planning new or modifying existing facilities.
- Measured the limits and characteristics of water recovered from an amine-based carbon capture system under conventional firing with air and oxy-fired conditions.
- Validated the design of a novel power plant steam condenser that incorporates significant potential for water savings compared to conventional all-wet designs.

Developed Novel Pollution Control Technologies for Mercury and Hazardous Air Pollutants (HAPs)

- Demonstrated mercury control technologies for challenging fuel types and plant configurations.
- Validated options available to detect and quantify low levels of HAPs.
- Developed a novel, cost-effective sampling method that measures multiple pollutants simultaneously.

Performed World-Class Outreach and Dissemination of Research Results to Industry Partners and Other Stakeholders

- Developed and conducted world-renowned conferences and workshops that brought together thousands of stakeholders to network and exchange timely information on air quality issues.
- Developed a Web-based GIS application to provide stakeholders with a tool to make informed decisions on improving oil and gas production in the Bakken petroleum system.
- Produced and broadcast a video documentary to showcase key issues related to the interdependence of water and energy.
- Developed and conducted a coal gasification short course targeting utility and other industry technical professionals.

This 10-year program (May 1, 2008 – May 31, 2018) merged two previous 10-year agreements—DE-FC26-98FT40320 (Base Agreement) and DE-FC26-98FT40321 (Jointly Sponsored Research Program)—into a single follow-on agreement. The Fossil Energy cooperative agreement between DOE and the EERC was initiated in 1983 when the EERC—then a DOE federal energy technology center—was defederalized and became part of UND. This dynamic 35-year partnership has provided critical and strategic technology development to address research needs in the DOE Office of Fossil Energy research programs while serving the missions and exploiting the strengths of both organizations through this agreement and a new 5-year Fossil Energy-Related Resources cooperative agreement established in 2015 (No. DE-FE0024233).

PROGRAM GOAL AND OBJECTIVES

The Joint Program on Research and Development for Fossil Energy-Related Resources is an excellent model for research, development, demonstration, and commercialization partnerships between government, industry, and the applied science and engineering communities to bring cutting-edge science closer to commercial application. The *overarching goal* of the program was to support DOE Fossil Energy goals by advancing the scientific knowledge and technical development essential to ensuring future sustainable supplies of affordable energy and clean water, protecting and restoring the environment, and reducing dependence on foreign energy sources, thereby increasing U.S. energy security. The *strategic objective* was to advance continued use of domestic fossil fuels as a mainstay of U.S. energy production by making fossil energy systems nonpolluting and more efficient, capturing and sequestering greenhouse gases (GHGs), and integrating the use of fossil and renewable energy sources into the energy mix. The research achievements from this partnership have exceeded these goals and objectives by contributing substantially to the development of science-based energy and environmental policy, educational foundations for science and technology, and commercialization and international marketing of energy technologies.

PROGRAM ORGANIZATION AND STRUCTURE

This program included basic/applied fossil energy research projects that spanned low, middle, and high technology readiness levels. Overall cost share to projects in this program has approached 40%, significantly exceeding the 29% overall requirement. This level of cost share indicates strong involvement and commitment from industry partners. Projects were cost-shared in the form of cash and/or cash-equivalent that met all criteria required by Office of Management and Budget (OMB) Circular A-110.

Projects complementary to DOE's program were chosen to bridge the gap between basic/applied research and technology development to accelerate the scale-up, demonstration, and commercialization of new and improved technologies. Approval of funding by DOE and nonfederal sponsors on a project-by-project basis ensured that the work performed had DOE program strategic significance and practical application in the private sector.

Continuation applications put forth research plans that addressed a variety of energy resources and related environmental issues, expressly recognizing the binding relationships that exist between recovery and use of resources, environmental impacts on ecosystems and watersheds, and the physical and economic security of the United States. The program provided flexibility to change the scope and content of research significantly from year to year to respond to DOE program priorities, evolving market needs, and available funding.

This program comprised Tasks 1.0–6.0, based on six strategic areas of focus that contributed directly to and programmatically fit with DOE Fossil Energy goals and exploited the EERC's unique background and capabilities in low-rank coal (LRC) applications, as well as an overall project management task (7.0), as detailed below.

TASKS/STRATEGIC AREAS OF FOCUS

Task 1.0 – Resource Characterization and Management focused on expanding the supply and use of domestic energy resources by characterizing their extent, properties, and recovery potential.

Task 2.0 – Climate Change and CO_2 Sequestration focused on advancing the development of new and improved technologies for capture and sequestration of carbon dioxide (CO_2) and other GHGs to provide cost-effective options for stabilizing and ultimately reducing GHG concentrations in the atmosphere while continuing to use domestic fossil fuels as a mainstay of U.S. energy production.

Task 3.0 – Alternative Fuels focused on advancing conversion processes for producing clean fuels and chemicals from the nation's abundant fossil resources to provide affordable energy for transportation and industry and to reduce dependence on imported oil.

Task 4.0 – Clean Power Systems focused on contributing strategically to the development of new and improved technologies for generating clean and affordable power from coal combustion and gasification, with an emphasis on the unique problems associated with using low-rank coals.

Task 5.0 – Water Management and Sustainability focused on understanding the impacts of resource extraction and use on the availability and quality of water and developing methods and technologies to minimize the water requirements of energy systems and the impacts of fossil fuel exploitation and use on water resources.

Task 6.0 – Strategic Studies focused on performing research on emerging concepts and technologies that might affect domestic energy supplies. Specific projects under this focus area were identified in consultation with DOE and industry stakeholders.

Task 7.0 – Project Management focused on ensuring the success of the program through experienced management and leadership related to the individual subtasks and to the program as a whole in coordination with the DOE Program Manager. Program results were communicated through technical presentations and peer-reviewed publications as well as contractually required reports.

Individual projects under Tasks 1.0 through 6.0 were assigned subtask numbers and funded under one or more of seven program areas through one or a combination of eight federal funding sources, as defined below.

Program Areas/Funding Sources

Cooperative Research and Development (CRD)/CRD supported fundamental and proof-of-concept studies based on scientific and engineering foundations for new and improved energy technologies and a wide array of related environmental issues. Because of the basic nature of the research, nonfederal cost share was not required for subtasks under this program area. Research funded under this program area had the potential to advance to the CRD Partnerships program area.

CRD Partnerships (CRDP)/CRD focused on more mature research that promoted the deployment of advanced technologies and concepts for improving energy efficiency and environmental performance. This research was beyond proof of concept, with significant cost share provided by nonfederal partners.

Strategic National Energy Security Solutions (SNESS)/Congressionally Directed Projects focused on identifying the most critical issues facing the U.S. energy industry and working with the private sector to develop methods and technologies to address these issues. Subtasks under this program area were cost-shared by nonfederal partners.

Innovations for Existing Plants (IEP)/IEP focused on the development and application of technologies to facilitate the existing domestic power generation fleet's ability to meet increased regulatory standards for clean air, specifically focused on CO_2 emissions, and clean water. Subtasks under this program area were cost shared by nonfederal partners.

Natural Gas and Oil (NG&O)/Strategic Center for Natural Gas and Oil focused on a broad spectrum of exploration and production and environmental issues associated with conventional and unconventional oil and gas resource development, including those associated with the Bakken shale of North Dakota and Montana. Subtasks under this program area were cost-shared by nonfederal partners.

Carbon Sequestration/Storage (CS)/CS and **Regional Carbon Sequestration Partnerships** focused on improving the understanding of factors affecting CO_2 storage permanence, capacity, monitoring, and safety in geologic formations and terrestrial ecosystems. Subtasks under this program area were cost-shared by nonfederal partners.

Carbon Capture (CC)/CC and **Postcombustion Capture** focused on increasing the efficacy while lowering the cost and energy penalty associated with CO_2 capture from large stationary sources. Subtasks under this program area were cost-shared by nonfederal partners.

A final breakdown of funding by program area/federal funding source and associated nonfederal cost share is shown below.

	Contractually Required			Actual Funding		
	DOE Share, $MM	Nonfederal Share, $MM	Total, $MM	DOE Share, $MM	Nonfederal Share, $MM	Total, $MM
Cooperative Research & Development	7.21	3.81	11.02	7.21	5.69	12.9
Congressionally Directed Projects	11.28	3.23	14.51	11.28	7.81	19.09
Innovations for Existing Plants	7.03	0.95	7.98	7.03	2.6	9.63
Strategic Center for Natural Gas and Oil	1.02	N/A	1.02	1.02	N/A	1.02
Carbon Sequestration	1.25	1.13	2.38	1.25	1.31	2.56
Regional Carbon Sequestration Partnerships	2.5	2.25	4.75	2.5	2.25	4.75
Carbon Capture	1.25	1.12	2.37	1.25	1.06	2.31
Postcombustion Capture	1.25	1.12	2.37	1.25	0.98	2.23
Total Funding	32.79	13.61	46.4	32.79	21.7	54.49
	71%	29%	100%	60%	40%	100%

Nonfederal partners in this program, 80 in all, included oil and gas industry stakeholders, energy companies, utilities, industry service organizations, state agencies, universities and other research entities, regional and local governments, technology vendors, and other private sector companies from the United States and across the world, as represented on the following page.

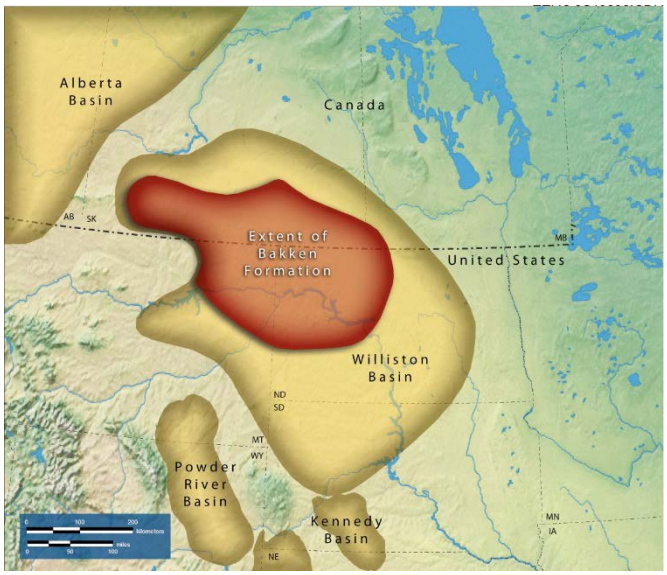

ACCELERGY
AECOM
AFR
ALBEMARLE
ALBERTA INNOVATES
ALCOA
Arthur J. Gallagher & Co. (AJG Coal, Inc.)
ATCO Power
BAKER HUGHES
BASIN ELECTRIC POWER COOPERATIVE
A Touchstone Energy® Cooperative
BLACK & VEATCH
Cansolv
CARBO CERAMICS
CATM Affiliates
CMG
CO2 SOLUTIONS
Constellation.
An Exelon Company
Continental RESOURCES
America's Oil Champion
CQuest
ENMAX
EPRI ELECTRIC POWER RESEARCH INSTITUTE
Eskom
Farmers Union
FMC
GEA
GE Global Research
GEI Consultants
GreatPoint ENERGY
GREAT RIVER ENERGY
HESS
HITACHI Inspire the Next
HUNTSMAN
ICCI Illinois Clean Coal Institute
iea International Energy Agency
ieaghg
KBR
KCRC
KINDER MORGAN
LEXTRAN
MarathonOil
metso
MIDWEST GENERATION
MINNESOTA CORN GROWERS ASSOCIATION
minnesota power
MONTANA-DAKOTA UTILITIES CO.
Nebraska Public Power District
Always there when you need us
NSG
NEUMANN SYSTEMS GROUP, INC.
NORTH DAKOTA CORN GROWERS ASSOCIATION
NORTH DAKOTA PETROLEUM COUNCIL
NorthWestern Energy
OHIO LUMEX
Prairie Public
Pratt & Whitney
A United Technologies Company
SaskPower
Schlumberger Carbon Services
SIPC
Standard Alcohol
SULZER
TAQA
Thermo SCIENTIFIC
TransAlta
Tri-Mer CORPORATION
UNIVERSITY OF WYOMING
XTO ENERGY
CO2 Capture Project Consortium
bp
Chevron
eni
PETROBRAS
Shell Canada Limited
SUNCOR ENERGY
PPL Montana
Portland General Electric
ppl
PACIFICORP
PUGET SOUND ENERGY
AVISTA
Northern Great Plains Water Consortium
American Crystal Sugar Company
CASS COUNTY GOVERNMENT
THE CITY OF Fargo FAR MORE
CITY OF GRAND FORKS
MOORHEAD MINNESOTA
Grand Forks County North Dakota
THE CITY OF EAST GRAND FORKS
Simplot
Xcel Energy®
RESPONSIBLE BY NATURE®

A DOE–EERC PARTNERSHIP SUCCESS STORY

The Joint Program on Research and Development for Fossil Energy-Related Resources encompasses a broad range of projects focused on resource characterization and management, climate change and CO_2 sequestration, alternative fuels, clean power systems, and water management and sustainability as well as strategic studies focused on emerging concepts and technologies of interest to DOE and industry partners. These projects build on the work of previous cooperative agreements and address the most timely and critical Fossil Energy priorities.

Key to the success of the DOE–EERC partnership is the ability to leverage federal dollars with industry cost share and the flexibility to evolve the program to meet market needs and address changing DOE priorities. Highlights of this 10-year program follow. All projects are detailed by subtask later in this report.

Oil and Gas Research Program



The oil and gas research program developed under this cooperative agreement focuses on efforts to support the development of unconventional tight oil resources in the Bakken Formation of the Williston Basin, which includes parts of Montana, North Dakota, Saskatchewan, and Manitoba. The Bakken Formation oil play is still in the early stages of development at a time when data collection, targeted investigations, and focused research are vital to improving and optimizing the ultimate production from the resource. As a play that is limited by low permeability and reliant on horizontal drilling and hydraulic fracturing, greater understanding of formation parameters is critical to improving production. Flaring has also been identified as an operational and environmental challenge for Bakken development, and the research program included activities to support industry efforts to reduce flaring.

Bakken Guidance

The EERC conducted a multidisciplinary research program to identify key attributes of successful Bakken wells and provide technically based guidance to stakeholders regarding future exploitation efforts (Subtasks 1.2 and 1.7). The EERC's Bakken research program has taken a four-pronged approach to evaluate and compare key attributes of the Bakken play in two North Dakota counties, Mountrail and Dunn. The research program focused on four topic areas: geology, geochemistry, geomechanics, and engineering. The evaluations were conducted largely through the use of a database of well-drilling, completion, stimulation, and production statistics and other

information developed under this program. In addition, laboratory data on the geochemical, mineralogical, and geomechanical properties from over 30 wells were generated.

Key conclusions reached based on the characterization activities include the following:

- Geologic characteristics appeared to have a strong influence on the hydrocarbon production rates for given areas within North Dakota that have similar completion practices.

- Production in Mountrail County greatly exceeded production in Dunn County and had significantly higher variability, with the higher production appearing to be linked to greater total organic carbon (TOC) and shale thicknesses, which, in turn, have the potential to create greater pore pressure-related fracturing.

- The presence of structural elements was consistent with areas of higher production.

- From an engineering perspective, results indicated multistage hydraulic fracturing consistently outperformed fewer-stage hydraulic fracturing when compared in proximity.

When this program was initiated in 2009, Bakken production was largely confined to three counties in North Dakota and one county in Montana. Based on the early characterization results from this program, in 2011 the EERC predicted that the Bakken play would expand to the southwestern, northeastern, and northwestern reaches of the basin in North Dakota. This prediction has come to pass, with present-day maps of Bakken fields showing an essentially continuous resource that includes producing wells in eight North Dakota counties.

Proppant Evaluation

The oil and gas research program also examined the effectiveness of different proppants used in hydraulic fracturing operations. Results of laboratory testing showed that highly concentrated fracture stimulations with ceramic- and sand-based proppants appear to be providing the best success for areas outside the Parshall and Sanish Fields. Targeting specific lithologies can influence production from both natural and induced fracture conductivity. Porosity and permeability are low, but various lithofacies units within the formation are highly saturated and, when targeted with appropriate technology, release highly economical quantities of hydrocarbons.

Wellhead Gas Utilization

In another Williston Basin-focused study, a project was conducted to demonstrate and evaluate the use of wellhead gas for fueling diesel engines used to power a drilling rig in North Dakota (Subtask 1.9). This evaluation consisted of two phases. Preliminary testing was conducted at the EERC using a leased engine and a mixture of diesel and simulated wellhead gas in a dual-fuel application. Phase II of the project consisted of field-testing engines using a mixture of diesel and wellhead gas on a drilling rig during the drilling of two wells. The results of the 47-day demonstration project illustrated that using wellhead gas in bifuel applications to power a drilling rig can lead to an overall decrease in diesel fuel use, fuel cost, and truck transport of liquid fuel without adversely impacting drilling operations. The specific results from this project included fuel-related cost savings of nearly $60,000 because of the lower value of wellhead gas relative to diesel and an increase in overall air emissions compared to diesel-only engine operation. If implemented broadly across the Williston Basin, bifuel operation of nearly 200 drilling rigs using otherwise flared wellhead gas could result in:

- 1,800,000 Mcf of wellhead gas used to power drilling rigs in 1 year (2% of currently flared wellhead gas).
- 18,000,000 gal of diesel fuel saved in 1 year.
- $72,000,000 of diesel fuel costs saved in 1 year.
- 3600 fuel delivery trucks (5000-gal tanker) avoided in 1 year.

Air emission reductions can be achieved using commercially available diesel engine exhaust gas treatment (catalytic conversion). These technologies are capable of reducing CO and nonmethane hydrocarbon emissions in bifuel-operated engines to levels similar to 100% diesel-only operation.

The oil and gas research program under this cooperative agreement produced over $2 million of funded research and teamed the EERC and DOE with oil and gas industry stakeholders in the Williston Basin. The results of the work performed under this agreement have led directly to a project to perform advanced characterization of unconventional oil and gas reservoirs to enhance CO_2 storage resource estimates and a study of rich gas EOR in the Bakken under the current 5-year DOE–EERC cooperative agreement.

Bakken CO_2 Storage and EOR Program

The use of CO_2 for EOR in tight oil reservoirs is a relatively new concept that could have major implications for the Bakken petroleum system, since even small improvements in productivity could increase technically recoverable Bakken oil by billions of barrels. The large-scale injection of CO_2 into the Bakken would also result in the geologic storage of significant amounts of CO_2.

Laboratory and Modeling Work

The EERC teamed with DOE and industry partners to conduct laboratory and modeling activities to examine the potential for CO_2 storage and EOR in the Bakken under this program (Subtasks 1.10 and 2.20). Specific activities included the characterization and modeling of North Dakota study areas as well as dynamic predictive simulations of possible CO_2 injection schemes to estimate potential CO_2 storage and EOR impacts. Laboratory studies were conducted to evaluate the ability of CO_2 to remove hydrocarbons from Bakken rocks and determine minimum miscibility pressures (MMPs) for Bakken oil samples. Results indicated that CO_2 can permeate the tight matrix of the Bakken and mobilize otherwise stranded oil, with CO_2 preferentially mobilizing lighter-molecular-weight hydrocarbons. Data from a CO_2 injection test conducted in the Elm Coulee area of Montana in 2009 were evaluated with an eye toward the possible application of knowledge gained to future injection tests in other areas. A first-order estimation of potential CO_2 storage capacity in the Bakken Formation in North Dakota was also conducted.

The results of the Phase I research activities suggest that CO_2 may be effective in enhancing the productivity of oil from the Bakken and that the Bakken may hold the ability to geologically store between 120 Mt and 3.2 Gt of CO_2. While there are no clear-cut answers regarding the most effective approach for using CO_2 to improve oil productivity or the storage capacity of the Bakken, the results underscore the notion that an unconventional resource will likely require unconventional methods of both assessment and implementation when it comes to the injection of CO_2.

Injection Testing

To verify and validate the findings of the laboratory- and modeling-based research efforts, in 2017, an injection test was conducted in a vertical well completed in the Bakken. The objectives of the test were to determine the injectivity of an unstimulated Bakken reservoir (i.e., a reservoir that had not been hydraulically fractured) and the ability of injected CO_2 to mobilize oil. The test

was conducted in a virgin Bakken reservoir. Preinjection and postinjection oil samples were analyzed for oil composition to determine the molecular weight distribution of the hydrocarbons.

Injectivity of the unstimulated Middle Bakken matrix was found to be low. Compositional analyses of the preinjection and postinjection oil samples indicate that the composition of the postinjection oil samples had greater amounts of lower-molecular-weight hydrocarbons than the pretest oils. Interpretation of the results from the field test suggest that although matrix injectivity is low, injected CO_2 can penetrate the Middle Bakken to mobilize oil from the matrix.

Past CO_2 injection tests in the Bakken were all conducted in horizontal, hydraulically fractured wells that used proppant to maintain the conductivity of the induced fractures. Those tests showed that injectivity into a stimulated horizontal Bakken well is not a problem. However, incremental oil was not produced, the mobility and fate of the injected CO_2 was not evaluated, and there is no evidence in publicly available data to suggest that a scientific approach was taken to evaluate the mechanisms controlling the ability of CO_2 to permeate the tight matrix and mobilize stranded oil. The use of a vertical well in a virgin reservoir reduced uncertainties associated with horizontal wells, such as the unknown distribution of rock properties and hydraulically induced fractures along the wellbore, which serve as preferential flow pathways.

The data generated by this field test support the findings of previous lab studies, which indicate that diffusion of CO_2 into the rock matrix may play a significant role in the use of CO_2 for EOR in the Bakken. The data from the field test have also been used in simulation modeling exercises to gain further understanding of the flow characteristics of CO_2 in unconventional tight oil formations. The results of this project provide field-based validation of previous laboratory- and modeling-based studies. They also provide valuable guidance toward the design and execution of future pilot tests in unconventional tight reservoirs. The results also provide insight into how laboratory-, modeling-, and field-based data can be transformed into plausible descriptors of larger-scale field observations, which, in turn, will yield improved understanding of the potential CO_2 storage resource and EOR opportunities associated with unconventional tight oil reservoirs.

Partnership for CO_2 Capture

Development of economically feasible carbon capture technology presents one of the biggest challenges to the fossil energy industry in the 21st century. Many existing technologies are capable of capturing CO_2 from coal-fired power plants, but most are expensive and inefficient. Development and evaluation of new technologies are critical steps toward economical CO_2 capture. To address this challenge, the EERC initiated a program to evaluate several CO_2 capture technologies that are among the most advanced under development. The Partnership for CO_2

Capture (PCO_2C) was formed with the overall goal of advancing the state of CO_2 capture by evaluating and demonstrating those technologies with the most commercial viability for utility applications. In performing pilot-scale testing of these systems, PCO_2C has identified the strengths and weaknesses of each technology to allow for enhanced performance and decreased costs for future applications.

Three-Phase Program

The PCO_2C Program was conducted in three phases under two subtasks (2.5 and 2.18). During Phase I, the focus was on understanding and developing two platform-based technologies: solvent-based absorption and stripping (postcombustion capture) and oxygen-fired combustion. Phase I results indicated that technological advances are the primary way to reduce the costs of capturing CO_2 using a retrofit oxy-fired technology. For postcombustion capture, 90% CO_2 capture can be achieved with monoethanolamine (MEA) and advanced solvents. However, the EERC has shown that the use of advanced solvents can be expected to reduce the cost of CO_2 capture considerably.

Phase II focused on further developing the most promising technologies studied in Phase I and used the information gathered in Phase I for the development of lower-cost and more effective capture technologies as well as their integration into a total system that provides substantial economic and environmental benefits. Phase III continued the work of Phase II by providing a platform for directly comparing the performance of various capture technologies to MEA performance, investigating flue gas precleaning technologies to remove contaminants that can reduce solvent life.

Phase III also expanded to include advanced precombustion membranes through the evaluation of membranes provided by a project partner, which led to several improvements in membrane construction. In Phase III, international involvement and cooperation continued, demonstrating the EERC's commitment to advancing capture technologies for a world with high power demands but doing so with a responsibility to environmental stewardship.

Advanced Gas Contactor

In a parallel project, the EERC evaluated an advanced gas contactor with the potential to significantly reduce the cost of postcombustion solvent-based CO_2 capture (Subtask 2.13). The system, which comprises a three-stage absorber and four-stage stripper, designed and built by a project partner and installed on the EERC's combustion test facility (CTF), uses a proprietary contacting technology that has been shown to reduce costs at the bench scale. Results showed performance improvement over traditional systems, with the specific surface area increased from

100 to 200 m^2/m^3 to almost 300 m^2/m^3. Additionally, increasing gas flow through the system showed no significant pressure penalty.

The PCO_2C Program under this cooperative agreement is rooted in and an offshoot of the work of previous cooperative agreements. This program involved nearly 30 nonfederal partners representing 36 industry organizations that provided nearly $4 million in cash and in-kind cost share. With DOE funding of nearly $8.6 million, this work represents over $12 million of funded research. Data generated from the PCO_2C Program led directly to advancement of two large-scale demonstrations by project partners, one of which is now preparing for commercialization at full scale. Additionally, two postcombustion solvent formulations were proven effective and are now being marketed worldwide.

Under the current Fossil Energy-Related Resources cooperative agreement, and as a direct offshoot of the work performed under the PCO_2C Program, DOE supported next-generation power cycles with integrated carbon capture (Subtask 2.1) to continue the advancement of precombustion membranes and identify the challenges of using supercritical CO_2 cycles with lignite coal. Other related projects under the current agreement include integrating carbon capture and storage (CCS) into North Dakota ethanol production (Subtask 1.3) and support of DOE carbon capture systems development and modeling (Subtask 2.3).

IEAGHG Partnership

The IEA Greenhouse Gas R&D Programme (IEAGHG) is an international collaborative research program established under the International Energy Agency (IEA) to evaluate technologies that can reduce GHG emissions from the use of fossil fuels. Members include 15 countries, the European Commission, OPEC (Organization of Petroleum Exporting Countries), and 16 multinational industrial sponsors. Under this DOE–EERC cooperative agreement, a key collaborative partnership was developed with IEAGHG on the globally important subject of geologic CO_2 storage. Geologic CO_2 storage has been suggested as one of the best potential methods for reducing anthropogenic CO_2 emissions to the atmosphere. The partnership forged with IEAGHG has led to critical advances in several topics related to CO_2 storage, including storage resource estimation, formation water extraction, and CO_2 transport.

CO_2 Storage Resource

As the field of CCS continues to advance and large-scale implementation of geologic CO_2 storage progresses, it is increasingly important to understand the potential of geologic formations to store meaningful amounts of CO_2. Identifying potential geologic sinks for CO_2 storage and developing reliable estimates of their storage resource/capacity are critical components of determining the efficacy of CCS. Through its cooperative agreement with DOE, the EERC partnered with IEAGHG to evaluate the methods by which storage resources are estimated (Subtask 2.8). Most of these methods involve a volumetric calculation of the pore volume of the target storage reservoir multiplied by a storage efficiency term. Three existing resource estimation

methods were examined, two for open systems (DOE and the Carbon Sequestration Leadership Forum [CSLF]) and one for closed systems. Storage coefficients were developed for both the DOE and CSLF methods at the formation level for different lithologies, and the site-specific level for different lithologies, depositional environments, and structures. The new storage coefficients developed over the course of this study can be used to move CO_2 storage resource estimates from a theoretical level to a more accurate one. This initial collaborative effort with IEAGHG greatly advanced the ability of technical researchers, government entities, and other stakeholders to estimate effective storage resource at levels ranging from site-specific to formation level. These results can be extrapolated to span large sedimentary basins and even entire nations and continents.

Building on the success of the initial study, a second effort investigating CO_2 storage resource estimation methods was initiated (Subtask 2.17). This collaboration with IEAGHG was focused on evaluating the real-world applicability of volumetric methods for estimating CO_2 storage resource. While these methods can be useful, they are not able to account for the effect of site-specific dynamic factors such as CO_2 injection rate, injection pattern, pressure interference between injection locations, and overall formation pressure buildup. To begin validating these volumetric methods, CO_2 storage resource estimates made using a volumetric method were compared with those estimated using dynamic reservoir simulation. Using reservoir simulation to estimate CO_2 storage resource allowed the dynamic effects from CO_2 injection to be taken into account. Two different deep saline formations (DSFs) in geographically separate locations were used to conduct the comparison. Results of the study show that the dynamic CO_2 storage resource potential is time-dependent and approaches the volumetric CO_2 storage resource potential over very long periods of time. Ultimately, the results indicate that volumetric assessments can be meaningfully used as long as the appropriate storage efficiency terms are used and it is understood that it will take many wells over very long time periods to fully realize the storage potential of a target formation.

The successful IEAGHG–DOE–EERC collaboration investigating CO_2 storage resource efficiency continued under the current cooperative agreement in the form of a Stage 2 study in which the focus was on practical storage efficiency factors.

Formation Water Extraction: Utility and Economics

The concept of extracting saline waters from reservoirs has been proposed as a means of managing storage formation pressures, increasing reservoir storage capacity, controlling CO_2 plumes, and controlling migration of displaced formation water. The practice may also provide water that can be put to beneficial use such as the supply of potable water where treatment can be performed at reasonable cost. In a third

collaborative effort with IEAGHG and DOE, the EERC conducted an analysis of the potential benefits of using formation water extraction during geologic CO_2 storage (Subtask 2.15). Specific project activities included a survey of geologic and water quality conditions of deep saline aquifers, selection of four case study sites representing a wide range of these geologic and water quality conditions, and a study of the impacts of formation water extraction on CO_2 storage and the potential for the beneficial use of extracted water at these sites. The four case study sites were the Ketzin site in Germany, the Zama Field in Canada, the Gorgon project area in Australia, and the Teapot Dome Field in the United States. Hypothetical reservoir-scale dynamic simulations were conducted to investigate the impact that formation water extraction could have on storage capacity and reservoir management and to determine effective water extraction rates for those purposes. Key outcomes are as follow:

- The increase in CO_2 storage capacity achieved by water extraction varies greatly based on site conditions.

- Benefits of water extraction in reservoir management include reduction of maximum reservoir pressures and plume management. In general, higher water extraction rates were required in order to provide better pressure and plume management.

- CO_2 storage resource is maximized by injecting supercritical CO_2, rather than mixing CO_2 into extracted water prior to injection.

- Most potential beneficial uses require water of significantly greater quality than is likely to be present in extracted water, thus requiring treatment. In most cases, the cost of desalination will be too high to make this a viable option.

The results of this effort showed that formation water extraction from CO_2 storage reservoirs is applicable for increasing storage capacity, reservoir pressure management, and plume control. Analysis of the resulting water quality and quantity, available treatment technologies, and potential transportation costs reveals there is likely to be limited potential for the beneficial use of extracted water from CCS facilities. Ideal circumstances of relatively high quality reservoir water and highly stressed or limited regional water resources will need to coexist before beneficial use of extracted water may be considered.

CO_2 Transport Considerations

CO_2 streams can vary substantially in terms of both composition and mass flow rate. The impact of this variation on pipeline and storage operation is not fully understood in terms of operability or infrastructure robustness. In a fourth collaboration with IEAGHG and DOE, a study was undertaken to compile real-world lessons learned about flexible operation of CO_2 pipelines and storage from both large-scale field demonstrations and commercial operating experience (Subtask 2.19).

The real-world results were obtained from two sources. The first consisted of five full-scale, commercial transport–storage projects: Sleipner, Snøhvit, In Salah, Weyburn, and Illinois Basin–Decatur. These scenarios were reviewed to determine the information available on CO_2 stream variability/intermittency for these demonstration-scale projects. The five projects all experienced mass flow variability or an interruption in flow. In each case, pipeline and/or injection engineers were able to accommodate any issues that arose. Significant variability in composition has not been an issue at these five sites. The second source of real-world results was telephone interviews conducted with experts in CO_2 pipeline transport, injection, and storage during which commercial anecdotal information was acquired to augment that found in literature. Experts represented a range of disciplines and hailed from North America and Europe.

Major outcomes of the study include the following:

- Compression and transport of CO_2 for EOR purposes in the United States are unlikely to experience impurity-related problems if CO_2 stream composition standards are maintained and pressures are kept at 10.3 MPa or higher.

- Cyclic, or otherwise intermittent, CO_2 supplies historically have not impacted in-field distribution pipeline networks, wellbore integrity, or reservoir conditions.

- The U.S. EOR industry has demonstrated that it is possible to adapt to variability and intermittency in CO_2 supply through flexible operation of the pipeline and geologic storage facility. This CO_2 transport and injection experience represents knowledge that can be applied to future CCS projects. A number of gaps in knowledge were identified that may benefit from future R&D, further enhancing the possibility for widespread application of CCS.

The Nexus of Water and Energy

Water is the world's most precious resource. The sustainable management of water is critical to the socioeconomic health of our country and the global community. For three decades, the EERC has investigated, developed, and demonstrated innovative, integrated approaches for water use and quality management through its cooperative agreements with DOE.

The electrical industry is second only to agriculture as the largest domestic user of water, accounting for about 40% of all freshwater withdrawals in the nation, with 90% used in fossil- and

nuclear-based electricity generation. To accommodate growing population and continued economic development, the United States will require ever-increasing amounts of energy and thus water to support growth. In addition, competition for water among the primary use sectors—agriculture, energy, industry, and municipalities—will increase. In areas where water resources are limited or become scarce as a result of overallocation and/or drought, competing interests for water could limit energy development and production. The questions related to adequate supplies of water for energy and all primary use sectors, as well as water conservation in each sector, are, therefore, receiving growing attention. The EERC is focused on the nexus of water and energy, and continues to work with DOE and corporate partners to evaluate alternate water supply sources for energy development and to reduce the water used in power systems.

Northern Great Plains Water Consortium

One of the approaches to bring together key energy producers and water users to address issues related to water availability, reducing freshwater use, and minimizing the impacts of facility operations on water quality was the development of the Northern Great Plains Water Consortium® (NGPWC) (Subtask 5.2). The over $8 million, 5-year consortium included 14 regional industry partners that provided nearly $5 million in nonfederal cost share. The overall goal of this effort was to assess, develop, and demonstrate technologies and methods to enhance water supply options, minimize water use, and reduce the discharge of water impacted by energy technologies, highlighting water management synergies that exist between energy-producing entities and the customers they serve. NGPWC undertook several individual projects focused on critical water supply and disposal issues in the Bakken shale oil play, techniques for recovering water from the drying of high-moisture coals, compiling information on critical water supply and use issues related to coal-fired power generation facilities, developing a documentary on the energy–water nexus, energy-saving opportunities for water treatment, advanced dry cooling technology as an alternative for power plants, and oil refinery water supply and treatment issues.

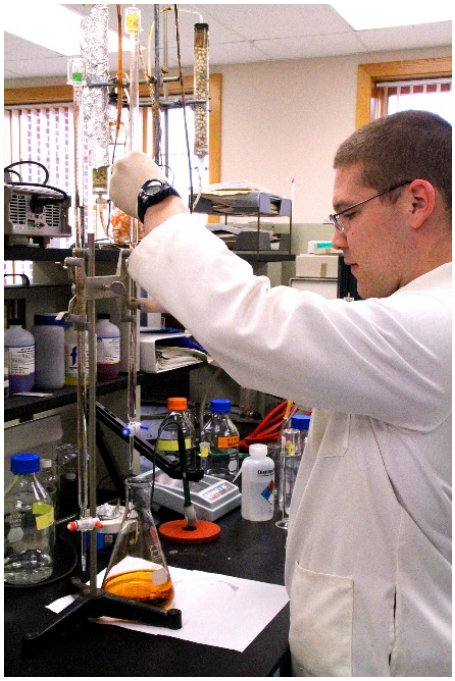
Web-Based Decision Support System

Gathering and tracking water supply and use data to support current and future initiatives continued (Subtask 5.1) as the EERC expanded a Web-based decision support system (DSS) initially developed under a previous cooperative agreement to provide power generation utilities with an assessment tool to address water supply issues when planning new or modifying existing facilities. The DSS integrates water and wastewater treatment technology and water law information with a GIS-based interactive map that links to state and federal water quality and quantity databases. This dynamic tool allows users to leverage and integrate knowledge of water and wastewater treatment technologies with the physical and spatial relationships of available water sources, competing uses, and current water demands. Expanded from a three- to an eight-

state region (North Dakota, South Dakota, Minnesota, Wyoming, Montana, Nebraska, Wisconsin, and Iowa) under this phase, the DSS provides a useful tool to a broader audience of not only power generation facilities but also other industry users and municipalities seeking new water resources or potential options for treatment and reuse of existing water supplies.

Water Minimization and CO_2 Capture

Under the Water and Energy Sustainability and Technology (WEST) Program developed under a previous cooperative agreement, the EERC evaluated water capture technologies in a CCS system and performed a complete systems analysis of the process to determine water minimization potential (Subtask 5.3). A pilot-scale liquid desiccant dehumidification system (LDDS), which is designed to extract water vapor from the air for use in cooling, was fabricated and tested in conjunction with a coal-fired combustion test furnace outfitted with CO_2 mitigation technologies, including the options of oxy-fired operation and postcombustion CO_2 capture using an amine scrubber. Important factors in the design were the flue gas flow rate entering the absorber as well as the temperature of the gas entering the LDDS.



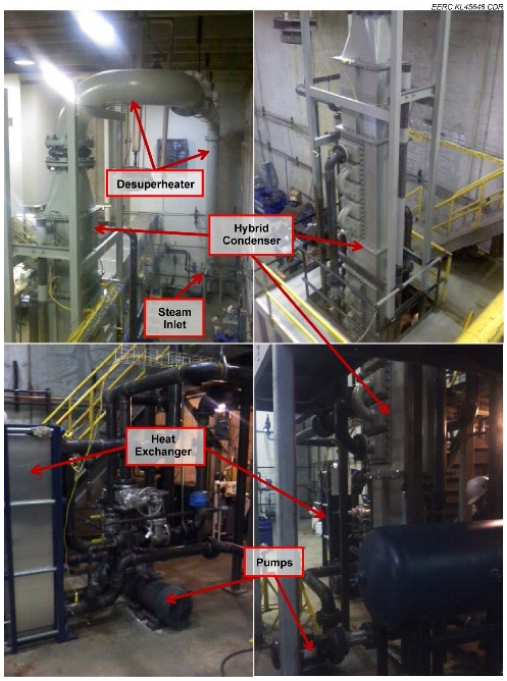
The water balance data from the pilot-scale tests showed that the packed-bed absorber design was very effective at capturing moisture down to levels that approach equilibrium conditions. Product water samples from the pilot-scale LDDS were routinely collected during test runs and analyzed for suspected contaminants. Compared to previous studies of moisture recovery from conventional coal flue gas, which were slightly acidic, the product water reclaimed from the CO_2 scrubber exhaust consistently had a high, basic pH, which is most likely a result of trace carryover of amine solution from the upstream CO_2 scrubber. An energy balance showed that very little preheating of the working fluid was accomplished in the condensing flue gas heat exchanger and, therefore, electric heat input was required for the majority of energy into the system. As a result, it was not possible to operate the system autothermally: that is, without external heat input. Examination of the operating conditions for the flue gas heat exchanger suggest it is unlikely that significant improvements could be made; however, the electric heat input could be reduced by installing a solution heat exchanger. In this heat exchanger, the hot, strong solution leaving the evaporator would be used to preheat the incoming weak solution.

When the LDDS was used to recover moisture from a concentrated CO_2 stream, CO_2 was partially absorbed because it is slightly soluble in aqueous solution. During shakedown tests of the pilot-scale LDDS under oxy-fired conditions, the desiccant solution was neutralized with a bed of $CaCO_3$, and in extreme cases, $Ca(OH)_2$ was added to raise pH. In terms of the most productive applications for the LDDS, higher-temperature, saturated gas flows offer the most promise. Not only does the maximum capture potential increase for the LDDS with increasing temperature, but

the available saturated water content increases dramatically with temperature. For the plant configurations of interest in this work—oxy-fired or conventional combustion with CO_2 capture—LDDS moisture recovery may be at a disadvantage since the process gas temperatures will be lower to accommodate either downstream CO_2 compression equipment or upstream amine-based scrubbers. Lower temperatures imply lower moisture content for recovery, which would tend to increase the levelized cost of LDDS water production.

The LDDS can feasibly recover a higher percentage of water than ambient-temperature condensation and can use low-temperature recovered heat for input energy, but it is a capital-intense approach. Novel integration strategies are needed to distribute the capital expenses among several power plant functions in order to make the LDDS concept more attractive. Identified strategies include making the absorber multipurpose, e.g., moisture absorption and polishing SO_2 control, recovering moisture from multiple process streams using common evaporator and condenser components and, possibly, sharing the plant's steam condenser to recover product water.

Novel Hybrid Condenser



In another effort to reduce utility water consumption, the EERC teamed with a technology developer to construct and test a first-of-its-kind hybrid condenser for cooling systems at electrical generation facilities to reduce water consumption beyond the capabilities of current hybrid cooling systems (Subtask 5.6). The pilot test system was built to test the operation of a small-scale model of the hybrid condenser design, combining the operations of a direct-contact jet condenser (used in dry/closed-loop cooling applications) and a surface condenser (used mainly in wet/open-loop cooling applications) into a single unit to effect condensation. Results showed the novel hybrid condenser design has the potential to significantly reduce overall investment costs up to 30% compared to all-dry, strictly closed-loop cooling technology; decrease water consumption up to 80% compared to conventional all-wet, strictly open-loop cooling systems; and increase performance compared to similar hybrid systems. The growing market for systems that conserve water and are easily retrofitted at existing power plants with strictly open-loop cooling systems where water resources have become limited provides a unique opportunity for commercialization of the hybrid condenser.

In all, nearly $10.7 million of research was funded through these efforts, with over $5 million of federal funding and more than $5 million of nonfederal cost share provided by the utility industry, technology developers, and regional stakeholders. The interconnected nature of energy and water systems and the ongoing challenges associated with diminished water supplies and the demands of the utility and other industries continue to be a focus of the DOE–EERC partnership.

Clean Power Systems: Addressing the Challenges of Fossil Energy Emissions

The EERC has pioneered the understanding of fossil energy air pollutants and other emissions and developed innovative measurement/control technologies for existing energy facilities through its partnership with DOE. This success has been built on the air quality control (QC) and assessment program developed under the previous cooperative agreement, with a focus on developing new and improved technologies for generating clean and affordable power from coal. Several projects related to the measurement and control of mercury and other HAPs were performed under this cooperative agreement and provide a strong scientific basis to support clean power systems.

One such program focused on the fate and control of mercury and trace elements in power systems that use CO_2 control technologies such as oxycombustion and gasification systems (Subtask 4.8). Additional projects addressed data gaps for systems that use conventional and multipollutant control technologies, such as electrostatic precipitators (ESPs), selective catalytic reduction (SCR) units, flue gas desulfurization (FGD) systems, and flue gas-conditioning methods. These additional programs supported the scientific basis for understanding mercury interactions, developing better control strategies and, in some cases, preventing mercury from being reemitted. This focused research also addressed stakeholder concerns and questions related to sampling and analytical methods for mercury, especially for continuous mercury monitors (CMMs) and sorbent trap (ST) methods for future compliance. Advances were made toward the development of a much simpler dry-based method for measurement of halogens and trace metals. A final key finding of this program relates to mercury and selenium concentrations/associations in freshwater fish, thereby potentially impacting health; this work has greatly enhanced the understanding of the second-order mechanism of mercury toxicity.

Sorbent-Based Mercury Control Technologies

In an effort focused on mercury control, the EERC undertook the evaluation of sorbent-based control technologies for an industry partner at a 403-MW unit that burns a high-ash, high-alkaline, relatively low mercury content subbituminous coal (Subtask 4.9). In this particular

combustion unit, the sorbent was injected ahead of the ESP, the only emission control device for the unit. Three mercury control approaches were evaluated: commercial untreated, treated activated carbons (ACs), and an approach using sorbent enhancement additives (SEAs) coupled with carbon-based and non-carbon-based sorbents. The testing was conducted with an overall mercury removal goal of ≥70%, which included baseline, parametric, and extended tests. The technologies that performed best were evaluated at 24-hr/day injection for 2 to 3 days to obtain more reliable performance. Mercury data were obtained using STs and CMMs. Parametric testing indicated that a treated AC reached a maximum mercury removal of 85%, while select SEA–sorbent combinations were able to achieve >90% mercury removal. Extended test results showed that each of the technologies tested could achieve ≥70% control (with many near 80% control) with a coal that had previously been shown to be problematic for mercury control. In addition, U.S. Environmental Protection Agency (EPA) Method 26a (M26a) was used to obtain data on halogen emissions, indicating slight increases for all mercury control technologies tested, although the levels did not exceed 2 ppmv. Although these were short tests, no observable negative balance-of-plant impacts were noted, including ESP performance, dust loading, and ash quality.

Another EERC study tested a tire-derived sorbent supplied by an industry partner to evaluate mercury removal performance using a low-sulfur coal flue gas in an EERC pilot-scale combustion facility (Subtask 4.19). AC was injected upstream of an ESP maintained at a temperature of 149°C (300°F). For comparison, a commercial AC was tested for mercury removal under the same flue gas conditions. A CMM and EPA M30B were used at the ESP outlet to monitor gaseous mercury emissions for each test condition. Under the test conditions of this study, the performance of the tire-derived carbon was slightly better than that of the commercial carbon for mercury capture.

In response to EPA's promulgation of National Emissions Standards for Hazardous Air Pollutants (NESHAPs) for the utility industry, the EERC undertook a program focused on determining the impact of a mercury control technology while sampling the HAPs targeted in NESHAPs. The HAPs included mercury, halogens, and other trace elements (Subtask 4.13). A full-scale demonstration was conducted at a power plant equipped with a particulate scrubber. Baseline sampling was conducted, followed by samples taken with a proprietary sorbent and a brominated AC (BAC). Results showed that the overall particulate removal was high and the two sorbents tested had little impact on particulate removal or opacity. Mercury removal near 30% was achieved with the proprietary sorbent and near 65% with BAC. In general, with the exception of mercury, >90% of all trace elements was removed by the wet particulate scrubber.

Mercury Concentration Measuring and Monitoring

An important need for U.S. plants is the ability to control and continuously measure mercury concentrations at less than 1.0 µg/m^3 while injecting mercury control technologies that contain bromine and other halogens. The EERC undertook a pilot-scale study to determine if bromine compounds and/or brominated carbons interfere with CMMs (Subtask 4.23). The project included 2 weeks of pilot-scale testing, one with natural gas and one with Wyoming Powder River Basin (PRB) coal. At the completion of testing: statistical analysis was performed to determine the accuracy of the CMMs as compared to ST samples at mercury concentrations ranging from 0.25 to 1.0 µg/m^3. The results showed that all instruments operated with little or no maintenance difficulties for the duration of testing. The Thermo Scientific CMM and ST results were nearly identical under all test conditions. However, when hydrogen bromide was part of the test matrix, the Tekran CMM results appeared to be biased low.

Additional low-concentration-mercury work was conducted to support state standards that would require 90% of the mercury to be removed, thus creating challenges with low-level mercury detection. A project was undertaken to evaluate both Tekran and Thermo Scientific CMMs in a pilot-scale system (Subtask 4.10). The project included 2 weeks of pilot-scale testing on natural gas using a mercury-spiking system and injection of SO_2, HCl, and O_2 and a third week of pilot-scale testing firing coal. At the completion of each week of testing, statistical analysis was performed to determine the accuracy and precision of the CMMs as compared to ST samples at different mercury concentrations ranging from 0.25 to 1.0 µg/m^3. The results showed that both instruments operated with little or no maintenance for 3 months. The Tekran and ST results were nearly identical under all test conditions. However, when coal was fired, the Thermo Scientific CMM results appeared to be biased high and were outside of a 20% relative standard deviation. This was not the case for the Tekran CMM. Therefore, after evaluating the instrument, Thermo Scientific repeated the test firing coal, and the results were improved.

Multielement Sorbent Trap

In 2011, the reference methods for trace metals and halogens were wet-chemistry methods, EPA Methods 29 (M29) and M26A. As a possible alternative to both, the EERC developed a novel multielement sorbent trap (MEST) method to be used to sample for trace elements and halogens (Subtask 4.24). STs offer a potentially advantageous alternative to wet-chemistry sampling methods, as they are simpler to use and do not require expensive, breakable glassware or handling and shipping of hazardous reagents. Testing was conducted at three different power plants, and the results indicated that for halogens, the MEST halogen (MEST-H) method did not show any significant bias compared to EPA M26A and appeared to be a candidate to serve as an alternative

to the reference method. For metals, the MEST metals (MEST-M) method offered a lower detection limit compared to EPA M29 and generally produced comparable data for Sb, As, Be, Cd, Co, Hg, and Se. Both the MEST-M and M29 encountered challenges associated with high blanks for Ni, Pb, Cr, and Mn. Although this issue has been greatly diminished through improved trap design and material selection, additional research is still needed to explore longer sampling durations and/or selection of lower background materials before MEST-M can be considered as an alternative method.

In another project to validate the MEST-H and MEST-M methods, the EERC performed field testing of the MEST methods against the EPA reference methods at two power plant units fueled by Illinois Basin bituminous coal (Subtask 4.27). For hydrochloric acid, MEST-H measured concentrations comparable to M26A at two power plant units, one with and one without a wet FGD (WFGD) scrubber. MEST-H provided lower detection limits for hydrochloric acid than the reference method. Results from a dry stack unit had better comparability between methods than results from a wet stack unit, which was attributed to the very low emissions in the wet stack as well as the difficulty of sampling in a saturated flue gas. Based on these results, MEST-H appears to be a good candidate to serve as an alternative to M26A or M26. For metals, MEST-M gave lower detection limits compared to M29 and produced comparable data for Sb, As, Be, Co, Mn, Se, and Hg for most test runs. However, the sorbent material produced elevated blanks for Cd, Ni, Pb, and Cr at levels that would interfere with accurate measurement at U.S. HAP emission limits for existing coal-fired power plant units. Longer sampling times employed during this test program appeared to improve comparative results for these metals. Although the sorbent contribution to the sample was reduced through improved trap design, additional research is still needed to explore lower-background materials before MEST-M can be considered as a potential alternative method for all of the trace metals.

H_2O_2 Injection-Based NO_x Emission Control

In response to interest in technologies to reduce NO_x emissions by the utility and small boiler industries, a chemical-manufacturing company licensed a technology using H_2O_2 injection to oxidize NO to NO_2 or higher oxidized forms. The oxidized form can then be easily removed in a wet or dry FGD. Although previous testing demonstrated the potential of this approach, much was unknown regarding the level of NO_x control that could be achieved for a spray dryer adsorption (SDA) FGD system. To help develop and prove the technology, the EERC partnered with the technology developer under this cooperative agreement to conduct pilot-scale tests using an SDA tower and fabric filter (Subtask 4.21). The primary goal of the work was to understand and improve NO_x capture as well as identify potential cobenefits of improved mercury capture. Although this technology will not achieve a high level of NO_x control (>90%), it has been shown to achieve 45%–50% control. There will almost certainly be niche markets for such a technology, for

example, power plants with low-NO_x burners and/or selective noncatalytic reduction systems that are already achieving 50%–75% control. For these plants, the addition of H_2O_2 to flue gas may provide the level of control mandated under current or proposed future regulations at a reasonable cost.

Over $8 million of research on the measurement and control of mercury and other HAPs was funded under this cooperative agreement. This work has allowed significant strides to be made to gain a better understanding of trace metals, other HAPs, improve sampling and measurement techniques, fill data gaps, address emerging technical issues, and develop and test control technologies that allow industry to cost-effectively meet regulatory standards.

Outreach: Beyond Technology Transfer

Integral to the success of a program of this magnitude is the communication of cutting-edge research results to industry partners and other stakeholders. Beyond contractually required reporting, results of individual projects were communicated through a variety of venues. International, national, and regional meetings, workshops, and conferences show-cased the work of this cooperative agreement, including the International Conference on Greenhouse Gas Control Technologies (GHGT); the Energy, Utility & Environment Conference (EUEC); and the Air & Waste Management Association's MEGA Symposium. Prestigious peer-reviewed and other journals such as *Energy & Fuels,* the *International Journal of Greenhouse Gas Control*, and *Energy Procedia* published the findings of these important studies.

Web-based information and research tools were developed to add value to project outcomes and provide a unique resource for decision makers and other industry stakeholders. A documentary was developed and broadcast on public television to showcase the challenges and opportunities of associated with the nexus of energy and water.

Coal Gasification Short Course

Much of the work of this and previous cooperative agreements has led to subsequent subtasks in new agreements to address issues that have come to light, data gaps, and partner needs, providing further value to DOE and industry. One such project involved the development of a coal gasification short course directed at utilities, independent power producers, and the petroleum and chemical industries (Subtask 4.2). The gasification short course targeted a technical audience and was designed to provide a broad understanding of gasification technologies and related

issues. The short course was presented at the EERC in Grand Forks, North Dakota, in 2009; in The Woodlands, Texas, in 2010; and in Melbourne, Australia, in 2013 to nearly 70 utility and other industry technical professionals.

Air Quality Conferences

The EERC's cutting-edge research on mercury and other HAPs began under previous cooperative agreements. In response to the need to share results with a broad audience of stakeholders, the EERC developed and held the inaugural conference on Air Quality (AQ): Mercury, Trace Elements, and Particulate Matter in 1998. Strategically sited in the Washington, D.C., area, the conference aimed to bring together industry stakeholders, government officials at all levels, environmental groups, and the research community to tackle timely issues and discuss impending regulation. With the support of DOE, EPA, the Electric Power Research Institute (EPRI), and other organizations, AQII–AQVI were held biennially, each expanding on the previous events and responding to industry trends and regulatory directives. Continuing these highly successful and sought-after events under this cooperative agreement, AQVII (Subtask 4.3) and AQVIII (Subtask 4.14) were organized and conducted.

AQVII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and three preconference workshops were held in 2009, with over 400 participants from 220 organizations representing 38 states, the District of Columbia, and 11 countries (with Canada represented by six provinces). An exhibit show featured 31 organizations involved in the air quality sector. AQVIII was held in 2011, again with over 400 participants representing 204 organizations, 39 states, the District of Columbia, and 18 countries. The sold-out exhibit featured 35 leading organizations in the air quality sector. Both conferences featured high-level keynote speakers, including congressional representatives, DOE and other federal agency officials, and representatives of industry groups such as the American Petroleum Institute (API). The AQ conferences and associated workshops brought together thousands of participants

representing industry, government, environmental groups, and the scientific and academic communities to network and exchange the most up-to-date information on air quality issues.

Bakken Decision Support System

The Bakken Decision Support System (BDSS), a Web-based GIS, was developed through the Oil and Gas Research Program under this cooperative agreement. The system assembles data for the Bakken and Three Forks Formations into a GIS application that enables users to visualize geologic and production information. Analytical tools support the evaluation and interpretation of geologic properties such as thickness, depth, structure, and organic content. Production data can be used to provide development history and identify areas of low or high production. The BDDS provides stakeholders with key information needed to make informed decisions to improve oil and gas production in the Bakken petroleum system.

NGPWC Outreach

NGPWC expanded its Web-based DSS, initially developed as an assessment tool for utilities to address water supply issues. The DSS now integrates water and wastewater treatment technology and water law information with a GIS-based interactive map that links to state and federal water quality and quantity databases, allowing users to leverage and integrate knowledge with the physical and spatial relationships of available sources, competing uses, and current demands.

In addition, NGPWC developed and produced a video documentary that showcases the key issues related to the interdependence of water and energy in the NGPWC region and beyond. “Water: The Lifeblood of Energy,” coproduced by Prairie Public Broadcasting (PPB), was broadcast in the PPB region, which includes North Dakota, northwestern Minnesota, southern Manitoba, and parts of Montana and South Dakota. This documentary not only provided added value to DOE and other consortium members, but also an opportunity to reach a broader, nonscience audience on the important topic of water and energy.

A hallmark of the EERC’s cooperative agreement with DOE is providing extra value to its partners. The important findings of this work were disseminated through technical reports, presentations, peer-reviewed publications, and other outreach opportunities across the globe.

Hands-on tools and other resources were developed to house results, engage stakeholders, and connect to new potential partners. The outreach component of the DOE–EERC cooperative agreement provides the essential link between the research, development, and demonstration of cutting-edge technologies and their commercialization and application worldwide.

CONCLUSION

This 10-year program comprised 75 individual projects that addressed six strategic areas of focus. In all, $32,798,698 of federal funding was leveraged with industry cash and in-kind cost share of $21,697,129 from 80 nonfederal partners for a total of $54,495,827 of funded research that:

- Advanced the development of unconventional tight oil resources in the Bakken Formation.
- Demonstrated the application of CO_2 Storage and EOR in tight oil formations.
- Developed advanced carbon capture technology.
- Addressed key application and infrastructure concerns for commercial deployment of CO_2.
- Demonstrated innovative, integrated water management strategies for energy development projects.
- Developed novel pollution control technologies for mercury and HAPs.
- Performed world-class outreach and networking of research results to industry partners and stakeholders.

These outcomes speak to the valuable return on the substantial investment in this program.

This DOE–EERC partnership success story is not the culmination of a 35-year relationship but, rather, a successful chapter in an ongoing, evolving collaboration. The next chapter, built on the solid foundation of this and previous cooperative agreements, is already being written, and its success will be defined by the cutting-edge research performed, the strength of the partnerships built with industry and other stakeholders, and the vision, shared objectives, and trust that embody the DOE–EERC partnership.

DETAILED SUBTASK SUMMARIES

This section of the report contains summaries of all individual subtasks. All projects are listed by task and subtask in the table that begins on page 29, followed by the detailed summaries.

Project Title	Subtask No.
Task 1 – Resource Characterization and Management	
Characterization of Erionite	1.1
Evaluation of Key Factors Affecting Successful Oil Production in the Bakken Formation, North Dakota; Phases I and II	1.2 and 1.7
Evaluation of Geophysical Technologies for Application to Carbon Capture and Storage	1.3
Biological In Situ Methane Production from Lignite	1.4
Development of Advanced Reservoir Characterization Techniques	1.5
Investigation of the Souring of Bakken Oil Reservoirs	1.6
Investigation of Improved Conductivity and Proppant Applications in the Bakken Formation	1.8
Demonstration of Gas-Powered Drilling Operations for Economically Challenged Wellhead Gas and Evaluation of Complementary Platforms	1.9
Task 2 – Climate Change and CO_2 Sequestration	
Assessment of the Feasibility of Geothermal Generation at CO_2 Geosequestration Sites	2.1
Creating a Numerical Technique for Microseismic Data Inversion	2.2
Geologic CO_2 Sequestration with Methane Farming	2.3
Integration and Synthesis in Climate Change Predictive Modeling	2.4
Partnerships for CO_2 Capture – Phases I–III	2.5 and 2.18
Assessment of Alternative Fuels on CO_2 Production	2.6
Transport Reactor for CO_2 Reduction in Lignite Coal and Subbituminous Coals	2.7
Development of Storage Capacity Coefficients for Carbon Dioxide Storage in Deep Saline Formations	2.8
Flame Characterization During Oxygen-Fired Combustion	2.9
Capitalizing on CO_2 Storage in Lignite Coal: Biological In Situ Methane Production	2.10
CO_2 Capture with Aqueous Froth	2.11
CO_2 Reduction by TiO_2	2.12
Evaluation of Novel Technologies for CO_2 Capture	2.13
Beneficial Use of CO_2 for North Dakota Lignite-Fired Plants	2.14
Extraction of Formation Water from CO_2 Storage	2.15
CO_2 Storage Efficiency in Deep Saline Formations	2.17
Operational Flexibility of CO_2 Transport and Storage	2.19
CO_2 Storage and Enhanced Bakken Recovery Program – Phases I and II	2.20 and 1.10
Task 3 – Alternative Fuels	
Electrochemical Hydrogen Production from Coal	3.1
Development of Next-Generation Coal-to-Liquid Catalysts	3.2

Continued . . .

Project Title	Subtask No.
Feasibility of Direct Coal Liquefaction in the Modern Economic Climate	3.3
Fischer–Tropsch Fuels Development	3.4
Catalytic Coal Liquefaction to Produce Transportation Fuels	3.5
Ammonia Production from Electricity, Water, and Nitrogen	3.6
Beneficiated Lignite Market Study	3.7
Analysis of Multiple Pathways for Converting Coal to Liquid Transportation Fuels	3.8
Direct Coal Liquefaction Process Development	3.9
Bench- and Pilot-Scale Evaluation of Processing Conditions and Catalyst for Syngas Conversion to Mixed Alcohols	3.10
Production of CBTL-Based Jet Fuels from Biomass-Based Feedstocks and Montana Coal	3.11
Gasification, Warm-Gas Cleanup, and Liquid Fuels Production with Illinois Coal	3.12
Task 4 – Clean Power Systems	
Feasibility of Hydrothermal Dewatering for the Potential to Reduce CO_2 Emissions and Upgrade Low-Rank Coals	4.1
Coal Gasification Short Course	4.2
Air Quality VII: An international Conference on Carbon Management, Mercury, Trace Elements, SO_X, NO_X, and Particulate Matter and Three Preconference Workshops	4.3
Intermediate-Temperature Alkaline Methanol Fuel Cell	4.4
Syngas Minicombustor: Enabling Trace Metal Analysis in Syngas by Conversion of Oxidized Form	4.5
Systems Engineering Study of Integrating Algae into Coal Combustion and Gasification	4.6
Fluid-Bed Testing of Catalyzed Feedstocks	4.7
Fate and Control of Mercury and Trace Elements	4.8
Full-Scale Testing of Sorbent Injection Technology for Mercury Control	4.9
Determining the Variability of Continuous Mercury Monitors at Low Mercury Levels	4.10
Testing of Modified Activated Carbon for Use in Hydrogen and Energy Storage	4.11
Algae Harvesting in an Integrated Power Plant–Algae System	4.12
Full-Scale Mercury Control Demonstration: ICR Sampling with Mercury	4.13
Air Quality VIII: An international Conference on Carbon Management, Mercury, Trace Elements, SO_X, NO_X, and Particulate Matter and Preconference Workshops	4.14
Performance of Eskom Coal in a Circulating Fluidized-Bed Combustor	4.15
Updating the "Improved Guidelines for Solving Ash Deposition Problems in Utility Boilers" Report	4.17
Testing of Indian Coal in a Transport Reactor Integrated Gasification (TRIG™) System	4.18
Pilot-Scale Mercury Testing for Advanced Fuel Research, Inc.	4.19
Testing of High-Ash Chinese Coal in a Transport Reactor Integrated Gasification (TRIG) System	4.20
Evaluation of a Spray Dryer Absorber for Multipollutant Control	4.21

Continued . . .

Project Title	Subtask No.
Extended Pilot-Scale Testing of the Pratt & Whitney Rocketdyne Compact Reformer	4.22
Pilot-Scale Testing Evaluating the Effects of Bromine Addition on CMMs at Low Mercury Concentrations	4.23
Field Evaluation of Novel Approach for Obtaining Metal Emission Data	4.24
Demonstration of Multipollutant Reduction Using a Lextran 3-in-1 Wet Scrubber	4.26
Evaluation of the Multielement Sorbent Trap (MEST) Method at an Illinois Coal-Fired Plant	4.27
Task 5 – Water Management and Sustainability	
Optimization of Cooling Water Resources for Power Generation	5.1
The Northern Great Plains Water Consortium	5.2
Water and Energy Sustainability and Technology (WEST)	5.3
Novel Thermal Storage for Power Plants	5.4
Technological Synergies for Recovery of Organic Pollutants from a Coal Seam at Garrison, North Dakota – Phase 2: System Operation and Performance Monitoring	5.5
Design and Pilot Plant Studies of Water Minimization Technology	5.6
Sediment Pore Water PAH-34 Method Validation and Field Demonstration	5.7
Electrochemically Promoted Microbial Hydrogen Production from Biomass and Wastewater	5.8
Finalizing ASTM Method and SRM Support	5.9
Testing of an Advanced Dry Cooling Technology For Power Plants	5.10
Task 6 – Strategic Studies	
Strategic Studies	6.1
Investigation of Two CO_2 Capture Strategy Concepts	6.2
Task 7 – Management and Reporting	
Management and Reporting	7.1

Task 1.0 – Resource Characterization and Management

Subtask 1.1 – Characterization of Erionite

Program Area:	CRD
Period of Performance:	7/1/08–1/31/10
Funding:	DOE: $60,000; Nonfederal: NA; Total: $60,000
EERC Subtask Manager:	Laura Raymond
DOE Technical Monitor:	Patricia Rawls
Nonfederal Partners:	NA
Final Report:	Eylands, K.E.; Azenkeng, A.; Mibeck, B.A.; Raymond, L.J. *Subtask 1.1 – Characterization of Erionite*; Final Report (June 25, 2008 – Jan 31, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-12-06; Energy & Environmental Research Center: Grand Forks, ND, Dec 2009.

Under Subtask 1.1, the EERC undertook an investigation to identify the potential presence of naturally occurring erionite in southwestern North Dakota in order to begin to assess the health risks associated with erionite exposure. Erionite, the naturally occurring, fibrous form of zeolite, is up to 800 times more carcinogenic than asbestos. Although erionite is no longer mined or marketed for commercial purposes, it can be a major component of other mined zeolite deposits. Zeolite deposits may also be associated with overburdens, posing a hazard during mining because of the possible presence of erionite. Zeolites are used globally in a variety of industrial applications, and as their use grows, the risk of erionite exposure is amplified and the health effects associated with mining and use as well as the lack of regulations and guidelines are of great concern.

Erionite-containing deposits were identified in a previous project because rocks were being mined for construction applications such as asphalt fill material and road base gravel. Prior analysis conducted by the EERC indicated the presence of erionite in outcrop, gravel pit, and road dust samples collected in Dunn County, North Dakota. Likewise, the major areas of zeolite formation and erionite deposits coincided with lignite- and subbituminous coal-mining areas. Disruption of these areas and overburden may create an increased risk of exposure without adequate precautions. The goal of this project was to identify the potential presence of erionite in collected samples from a much larger geographic area than previously sampled.

Samples containing erionite were found at several locations in Dunn, Stark, and Slope Counties as well as a single sample in Grant County (South Coffin Butte), North Dakota. X-ray diffraction (XRD)—the standard method for erionite detection—and scanning electron microscopy (SEM)—which allows visual and chemical detection—were both used. Several samples were found to contain erionite by SEM methods in concentrations too low to be detected by XRD. Conversely, samples in which the erionite was masked in clay, lumplike particles were identified by XRD methods and not visually imaged by SEM. This investigation demonstrated that positive identification of erionite cannot be achieved by the use of either of these methods alone and that they should be used in conjunction with each other to derive accurate results.

The results of this work indicate erionite occurrences were recognized as a constituent within a mappable rock unit or marker bed within a rock unit that can be identified and laterally correlated. Preliminary mapping of erionite distribution did not indicate a correlation between erionite occurrences and lung disease, but did indicate an increased cancer rate in some counties compared to national levels. A data bank was created for comparative analysis of different mineral compositions of erionite obtained from additional locations. The information developed in this project will enable better surveys for toxicological studies and risk assessments and is valuable to research on the health effects associated with erionite exposure and the use of zeolites.

Subtask 1.2 – Evaluation of Key Factors Affecting Successful Oil Production in the Bakken Formation, North Dakota

Program Area:	NG&O
Period of Performance:	10/1/08–3/31/10
Funding:	DOE: $496,340; Nonfederal: NA; Total: $496,340
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	John Terneus
Nonfederal Partners:	NA
Final Report:	Sorensen, J.A., Schmidt, D.D., Smith, S.A., Bailey, T.P., Mibeck, B.A.F., and Harju, J.A., 2010, Subtask 1.2 – evaluation of key factors affecting successful oil production in the Bakken Formation, North Dakota: Final report (October 1, 2008 – March 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, Grand Forks, North Dakota, Energy & Environmental Research Center, March.

Subtask 1.2 was the first phase of a research program to bring to the forefront data critical to the efficient development of the Bakken resource, focused on evaluating the key factors affecting successful oil production in the Bakken Formation in North Dakota. As a highly technical play limited by low permeability and fracture porosity, greater understanding of Bakken Formation parameters is paramount to unlocking tightly held hydrocarbons within the reservoir.

This research program took a four-pronged approach to evaluate and compare key attributes of the Bakken play in two North Dakota counties, Mountrail and Dunn. These counties were chosen as the study area because while some level of success has been seen in both counties, wells in Mountrail County have generally been more prolific producers than those in Dunn County. The premise of the project approach was that by comparing key geologic and engineering attributes of the two counties, insight would be gained that could improve the productivity of Dunn County wells and potentially provide guidance in exploring for and exploiting new subplays.

Broadly, the research program focused on four topical areas: geology, geochemistry, geomechanics, and engineering. Aspects of each were evaluated and compared between the two counties. Evaluations were conducted largely through the use of a database of well-drilling, completion, stimulation, and production statistics and information created under this project. In addition, a variety of laboratory-generated data on the geochemical and mineralogic composition

of chip samples from 26 locations and geomechanical properties of core samples from six locations were also developed and applied to the evaluations.

Results of Phase I research activities indicated that a greater understanding of the natural fracture network system of the Bakken was critical to improving production performance. Optimizing completion practices involving horizontal drilling and fracture stimulation is important to unlocking tightly held reservoir fluids. Horizontal drilling of the middle member of the Bakken coupled with multistage fracturing has outperformed all previously completed Bakken wells in North Dakota. However, geologic influences appear to dictate the hydrocarbon production rates for given areas within North Dakota that have similar completion practices. While more detailed geologic study was indicated to further support these preliminary conclusions, the following trends within the Middle Bakken Formation of Dunn and Mountrail County were identified:

- Production in Mountrail County greatly exceeded production in Dunn County and had significantly higher variability.

- The higher production of Mountrail County appeared to be linked to greater TOC and shale thicknesses, which together have the potential to create greater pore pressure-related fracturing.

- The presence of structural elements, although different in both Dunn and Mountrail Counties, was consistent with areas of higher production. The influence of these structural elements on the creation of both natural and operationally induced fracture systems may be their major contribution to successful production.

- Higher production within Dunn County was associated with the area along the Heart River Fault, which coincides with an area of high original TOC content.

- Lithology could potentially play a role in oil mobility, an improved understanding of which may serve to guide the design of stimulation practices and provide insight regarding future exploration efforts.

- Multistage fracture completions appeared to outperform lesser-stage completions when compared in proximity. It appeared that at least in some areas, multistage hydraulic fracturing should improve the chances of greater oil production.

- Various multilateral wells did not appear to gain significant production advantage despite lower per-foot drilling costs.

- Well azimuth, although relevant to the direction of principal stress, did not appear to be a factor in oil production.

- Longer lateral wells appeared to produce more oil when compared to shorter laterals within proximity.

This research program continued under Subtask 1.7 – Evaluation of Key Factors Affecting Successful Oil Production in the Bakken Formation, North Dakota – Phase II.

Subtask 1.3 – Evaluation of Geophysical Technologies for Application to Carbon Capture and Storage

Program Area:	CRD
Period of Performance:	3/1/10–2/28/11
Funding:	DOE: $90,000; Nonfederal: NA; Total: $90,000
EERC Subtask Manager:	John Hamling
DOE Technical Monitor:	Norman Popkie
Nonfederal Partners:	NA
Final Report:	Hamling, J.A., Bremer, J.M., Lindeman, C.D., Klapperich, R.J., Smith, S.A., Sorensen, J.A., Steadman, E.N., and Harju, J.A., 2011, Subtask 1.3 – evaluation of geophysical technologies for application to CCS: Final report (March 1, 2010 – February 28, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2011-EERC-02-09, Grand Forks, North Dakota, Energy & Environmental Research Center, February.

The objective of Subtask 1.3 was to provide those involved in the planning and implementation of large-scale CO_2 storage projects with an objective and comprehensive resource for critical information on the applicability of a variety of geophysical technologies to site characterization and monitoring, verification, and accounting (MVA) of injected CO_2. The deliverables of this project provide the information necessary to support decisions and facilitate communications between CO_2 storage operators and geophysical service providers.

The project comprised four distinct activities:

- Evaluation of downhole wellbore geophysical technologies
- Evaluation of surface and combined surface and downhole geophysical technologies
- Development of a geophysical database
- Technology transfer

Twenty-two commercially available geophysical technologies were evaluated, and fact sheets were developed for each. The fact sheets provide a comprehensive, objective source that considers the specific applicability of each technology to CO_2 storage. They were designed to supplement DOE's *Best Practices for: Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations* by expanding each geophysical technology measurement category into a working document that can be quickly referenced for high-level assessments. Fact sheet development involved the following:

- Information was obtained from publicly available literature, sales material, interviews with service providers, technical papers, and journal articles. Generic terminology and cross-referencing were used to minimize service company bias where applicable.

- Each fact sheet consists of an operational overview, applications, deployment logistics, tool limitations, sources of measurement error, lead time to deploy technology, overview of selected case studies, price estimates, and references.

- To facilitate fact sheet development if a common or novel application, tool limitation, or source of error was listed for a technology, it was included in that technology's fact sheet. A variety of similar geophysical technologies and tools are available from most service providers and between various service providers. This work did not compare and contrast measurements between tools or service companies; rather, it provides an overview of available technologies.

- Certain geophysical technologies require data processing or interpretation, which may require supplementary data. Although applications for each measurement category are presented, specifics on the interpretation methodologies from the tool output are not detailed nor are supplementary data requirements, as they can be highly site- or processing-specific, which was beyond the scope of this project.

- Many tool limitations and sources of error are listed as a method of QC so that they may be addressed prior to technology deployment; however, they may not be applicable in many circumstances. Many service companies address and correct these issues during data acquisition or processing; therefore, this may be a nonissue.

- Price estimates are presented for comparative purposes only. Pricing can fluctuate drastically and is affected by many variables, both technical (such as depth, reservoir pressure, measurement resolution) and nontechnical (such as geographic location, the oil and gas market within a given region). Price estimates were compiled from a variety of service providers, both through the course of this project and from previous EERC experience, and are based on a generic North Dakota deployment in 2010.

- Fact sheets were peer-reviewed by three major oil and gas industry geophysical service providers—Schlumberger, Baker Hughes, and Pinnacle, a Halliburton Company.

Technology, interpretation techniques, and best practices are constantly evolving within the oil and gas as well as the emerging CO_2 capture and sequestration industries. While this work provided assessments of individual technologies, it was designed primarily to facilitate informed discussions between geophysical service providers and CO_2 storage stakeholders. The fact sheets developed provide a tool that could be considered along with the many other factors involved in the decision-making process regarding geophysical technologies for each unique project.

Subtask 1.4 – Biological In Situ Methane Production from Lignite

Program Area:	CRD
Period of Performance:	7/1/09–6/30/11
Funding:	DOE: $120,000; Nonfederal: NA; Total: $120,000
EERC Subtask Manager:	Darren Schmidt
DOE Technical Monitor:	Steven Markovich
Nonfederal Partners:	NA
Final Report:	Schmidt, D.D. *Subtask 1.4 – Biological In Situ Methane Production from Lignite*; Final Report (July 1, 2009 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-19; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

Under Subtask 1.4, a study was conducted to consider microbially enhanced coalbed methane (CBM) production from a CO_2 sequestration pilot test conducted in a lignite coal reservoir in North Dakota. Coal seams are a potential target for geologic sequestration of CO_2. The injection of CO_2 into coal has the potential to produce methane, referred to as enhanced coalbed methane (ECBM), the mechanisms of which include the injection of gases (CO_2/N_2) into a coal reservoir, adsorption of the injected gas onto the coal, desorption of methane, and production of gas through a well to the surface. Further enhanced methane production was considered by means of microbial activity in the coal reservoir. At the time of this study, microbially enhanced CBM was considered to have the potential to increase domestic sources of natural gas and was the frontier technology in CBM.

The focus of the study was to consider potential revenue-generating strategies for coal-based carbon storage projects. Laboratory work was designed to address potential hurdles related to the CO_2 environment at reservoir conditions. The challenges included the low temperature (55°F), which tends to slow the rate of methane production from anaerobic bacteria, and the high-pressure environment (350 psi), which contributes to greater dissolved CO_2 and lower pH, which can inhibit microbial activity. A pilot test included stimulation of the CO_2–coal reservoir by pumping 200 bbl of a formulated microbial fluid followed by monitoring of gas production.

Microbial enhancement for CO_2 sequestration is challenging, both economically and technically. The field results of this study did not produce appreciable methane. Laboratory methane production experiments at reservoir conditions proved that the challenges of low temperature and high pressure can be overcome and that production is likely to be 4 orders of magnitude lower than typical anaerobic production in surface reactors. Economic analysis revealed that the capital cost to drill wells is a significant cost implication and that a successful cash-positive outcome for this technology would require a credit for receiving waste to eliminate hauling costs. The advantage of subsurface microbial methane production is the potential for large volumes of fluids to incubate and produce cost-effectively in situ.

Subtask 1.5 – Development of Advanced Reservoir Characterization Techniques

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $120,000; Nonfederal: NA; Total: $120,000
EERC Subtask Manager:	Steven Smith
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Smith, S.A., Azenkeng, A., Mibeck, B.A.F., Hurley, J.P., Eylands, K.E., Sorensen, J.A., and Harju, J.A., 2011, Subtask 1.5 – development of advanced reservoir characterization techniques: Final report (June 15, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement DE-FC26-08NT43291, EERC Publication 2011-EERC-06-23, Grand Forks, North Dakota, Energy & Environmental Research Center, June.

Subtask 1.5 investigated methods to improve the ability to estimate the porosity of rock samples representative of geologic formations known to contain hydrocarbons or that are considered good candidates for CO_2 storage. The determination of the physical properties of rocks, including mineralogy, grain geometry, grain relationships, and bulk volume, plays a critical role in the characterization phase of oil and gas exploration activities. The injection of CO_2 into deep geologic formations has been considered as a means of reducing CO_2 emissions to the atmosphere. The characterization of geologic formations, whether they are reservoirs for hydrocarbons or CO_2, rely on the use of specialized techniques to describe qualitatively and quantitatively the structure and fabric of the rock. One such technique includes the bombardment of a rock sample with x-rays using an instrument known as QEMSCAN® (Quantitative Elemental Mapping by Scanning Electron Microscopy).

QEMSCAN is a fully automated microanalysis system that outputs digital mineral maps of an entire 2-D sample surface (~30 mm in diameter) while significantly reducing the time required for the acquisition of data. Information on the sample, including the size, shape, and area of each mineral grain, can be obtained for the entire surface area scanned or on a particle-by-particle basis. Previous work identified limitations in the outputs of the instrument. One such limitation involves the underestimation of pore space in rock samples analyzed after using standard coating and polishing preparation techniques. A second limitation involves the identification of accessory minerals, which are important indicators of depositional setting and diagenetic history of rocks. In this project, methods were investigated to improve the ability to estimate the porosity of rock samples using QEMSCAN.

Analyses were performed on samples collected from seven geologic formations within the Williston Basin and/or PRB. The formations from which samples were collected represented a broad range of clastic and carbonate rock types. Ceramic materials developed by the EERC were also analyzed using QEMSCAN techniques. Porosity measurement estimates were improved significantly compared to estimates made using traditional QEMSCAN analysis. Four methods were evaluated in this work, each of them encountering slight limitations that were easily

overcome. The techniques explored will improve the ability of QEMSCAN to determine the porosity of reservoir rocks and identify accessory minerals over traditionally derived QEMSCAN measurements through the use of new image analysis techniques and improved coating and polishing sample preparation. All estimates of porosity were compared against gas pycnometry measurements and analyzed using an optical profiler to validate pore area-to-pore volume measurements. The QEMSCAN techniques developed over the course of this project were also effective in the analysis of key properties of ceramic materials. Lessons learned over the course of project activities included the following:

- Sample preparation techniques strongly influence the results of QEMSCAN analysis.
- QEMSCAN is particularly useful as part of a suite of analytical methods.
- QEMSCAN can add significant value to studies that require both chemical and structural information.
- Method development using an appropriate sample set and complementary analytical techniques can add value to existing laboratory capabilities.
- The interpretation of QEMSCAN results must take into account the nature of sample preparation.

The results of this work will provide stakeholders with improved methods for deriving pore volumes in rock samples and greater understanding of materials analysis techniques using QEMSCAN.

Subtask 1.6 – Investigation of the Souring of Bakken Oil Reservoirs

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $130,000; Nonfederal: NA; Total: $130,000
EERC Subtask Manager:	Steven Smith
DOE Technical Monitor:	Sinisha Jikich
Nonfederal Partners:	NA
Final Report:	Smith, S.A., Holubnyak, Y.I., Kurz, B.A., Sorensen, J.A., and Harju, J.A., 2011, Subtask 1.6 – investigation of the souring of Bakken oil reservoirs: Final report (June 15, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2011-EERC-06-20, Grand Forks, North Dakota, Energy & Environmental Research Center, June.

In Subtask 1.6, a series of modeling exercises were conducted to understand the mechanisms that may lead to souring of wells in the Bakken Formation. Advances in drilling and completion techniques, coupled with favorable oil prices, have allowed field operators to aggressively pursue exploration in the Bakken. Oil quality is generally considered sweet, meaning that it is low in

sulfur. However, anecdotal evidence indicated that sudden and sporadic souring (increased occurrence of hydrogen sulfide) of Bakken crude has been observed in a few wells. There are several potential mechanisms for souring of previously sweet reservoirs, but the issue is not well understood in this highly complex play. This research examined two abiotic pathways for the souring of a reservoir: 1) production of H_2S as a result of geochemical reactions between introduced fluids and formation mineral constituents and 2) production of H_2S as a result of fluid intrusion from the overlying Lodgepole Formation into the Bakken Formation.

A series of numerical modeling exercises were conducted to examine the extent to which geochemical and/or geomechanical factors influence the generation of H_2S within the Bakken Formation. Geochemical modeling scenarios suggest that H_2S production within the Bakken can be triggered in the presence of the mineral anhydrite. Mineral analysis of the formation indicates that concentrations of anhydrite are low and, as such, make this an improbable factor in the generation of observable quantities of H_2S. Geomechanical modeling of hydraulic fracturing indicated that migration of H_2S from the Lodgepole–Lower Madison Formations is possible as a result of fracture migration through the Upper Bakken. However, if migration of fluids was occurring from overlying formations, a noticeable increase in water production should logically follow, but increased water production has not generally been observed.

Over the course of this investigation, significant progress was made in furthering the understanding of this issue. While both options investigated are viable means of producing significant quantities of sulfur in this reservoir, neither can be correlated directly to the limited observations at the time of this study. Future evaluations will be enhanced greatly as additional water chemistry and well-souring data become available through targeted field studies and laboratory activities.

Key lessons learned from this evaluation include the following:

- No strong correlation exists between the geologic setting and the souring of select wells observed in this study.
- Because publicly available well files did not include information on whether souring had occurred, it was not possible to specifically correlate souring with possible increases in water production that would be indicative of a fracture into the Lodgepole Formation.
- Pyrite oxidation reactions were found to be thermodynamically impossible under Bakken reservoir conditions.
- A clear correlation appears to exist between a drop in reservoir pressure and H_2S production.
- Further site-specific data collection will greatly improve the understanding of this issue.

Subtask 1.7 – Evaluation of Key Factors Affecting Successful Oil Production in the Bakken Formation, North Dakota – Phase II

Program Area:	NG&O
Period of Performance:	5/1/10–10/31/11
Funding:	DOE: $522,670; Nonfederal: NA; Total: $522,670
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	John Terneus
Nonfederal Partners:	NA
Final Report:	Schmidt, D.D., Smith, S.A., Sorensen, J.A., Knudsen, D.J., Harju, J.A., and Steadman, E.N., 2011, Subtask 1.7 – evaluation of key factors affecting successful oil production in the Bakken Formation, North Dakota – Phase II: Final report (May 1, 2010 – October 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, Grand Forks, North Dakota, Energy & Environmental Research Center, November.

Subtask 1.7 continued and expanded on the multidisciplinary research program undertaken in 2008 (Subtask 1.2) to identify key attributes of successful wells in the Bakken Formation and provide technically based guidance to stakeholders regarding future exploitation efforts. This project focused on five topical areas: geology, geochemistry, petrography, geomechanics, and engineering.

While Phase I work focused on aspects of Mountrail and Dunn Counties and indicated that geologic factors and engineering practices both played critical roles in determining the likelihood of success for any given Bakken well, Phase II efforts looked more broadly across the North Dakota portion of the Bakken play. The results of the Phase II work centered on well completions, productivity, and geologic factors indicative of productivity, such as geochemistry-related oil saturation, geomechanical properties related to the design of hydraulic fractures, and petrography for characterization of the rock fabric.

Key findings of the Phase II work include the following:

- Production in the Bakken–Three Forks Formations clearly benefits from multistage hydraulic fracturing. Completion data collected from over 700 wells definitively enumerate the engineering aspects of the play and suggest that there is room to further improve stimulation treatments with quality proppants and shorter treatment spacings along the lateral wellbore.

- Water and oil saturation data coupled with water-cut data appear to be useful in identifying and evaluating productive and nonproductive areas along the eastern edge of the Bakken play. The correlation appears to be less applicable to production in the western portion of North Dakota, although more saturation data would be necessary to fully evaluate this concept.

- The majority of identifiable porosity in thin-section samples was in partially healed microfractures or residual hydrocarbon-filled accumulations.

- Pore structures in thin sections were observed to be highly disconnected, while intragranular permeability was highly compacted and cemented. This supports the observation that productivity has historically been attributed to natural and/or induced fractures.

- Areas of North Dakota that have highly productive lithofacies within the Middle Bakken tend to comprise geomechanically weaker rocks. Brittle rocks with high Young's modulus tend to propagate longer fractures.

- The strength of Middle Bakken rocks appears to be related to microstructure and facies. Structureless and weakly laminated samples tend to display higher peak strength, whereas strongly laminated or chaotically bedded samples are weaker.

- Geomechanical properties in the Three Forks Formation vary widely because of the highly laminated nature of the rock. When not highly laminated, Three Forks rocks can have higher strengths than Middle Bakken rocks.

- With respect to peak strength in the Bakken Formation, sample data consistently fall in the 45,000-psi area, although the actual range is 18,000–58,000 psi. Depth is not a significant factor affecting mechanical strength, although deviations from the norm appear to be tied to microstructure and/or facies.

- Examination of data from horizontal wells in which the wellbore treatments target softer rocks suggests that proppant placement in the near-wellbore requires critical attention to maintain good conductivity of fluids from the formation.

Technological advancements, particularly related to hydraulic fracturing, continue to unlock greater tight oil resources, and expansion of the Bakken–Three Forks play in North Dakota continues to develop. With the size of the recoverable resource in the range of several billions of barrels, there will continue to be opportunities to drill wells and pursue untouched hydrocarbons through improved stimulation practices or EOR operations.

Subtask 1.8 – Investigation of Improved Conductivity and Proppant Applications in the Bakken Formation

Program Area:	CRDP
Period of Performance:	5/1/11–7/31/12
Funding:	DOE: $113,201; Nonfederal: $209,856; Total: $323,057
EERC Subtask Manager:	Bethany Kurz
DOE Technical Monitor:	John Terneus
Nonfederal Partners:	CARBO Ceramics and North Dakota Industrial Commission (NDIC) Oil and Gas Research Program
Final Report:	Kurz, B.A., Schmidt, D.D., Smith, S.A., Beddoe, C.J., Lindeman, C.D., and Mibeck, B.A.F., 2012, Subtask 1.8 – investigation of improved conductivity and proppant applications in the Bakken Formation: Final report (May 1, 2011 – July 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2012-EERC-08-04, Grand Forks, North Dakota, Energy & Environmental Research Center, August.

Subtask 1.8 involved an investigation of ways to improve the understanding of proppant performance and the factors that contribute to hydraulic fracture conductivity loss in the Bakken Formation of North Dakota, a significant portion of the largest contiguous oil reserve ever discovered in the lower 48 states. The U.S. Geological Survey's (USGS's) original study of the Bakken found 4.3 Bbbl of recoverable oil in the Montana and North Dakota portion of the Williston Basin. According to federal testimony provided by the director of the North Dakota Department of Mineral Resources, "Hydraulic fracturing is a critical component of developing the Bakken Formation, indeed every shale play throughout the U.S. and Canada. Without hydraulic fracturing, under regulation of the states, this resource could not be produced" (1).

Hydraulic fracturing is the process of improving the ability of oil to flow through a rock formation by creating fractures. The process involves pumping a mixture of water and additives into the fracture that includes various sizes of sand or ceramic particles called proppants, which are designed to "prop" the fractures open, creating greater conductivity of fluids to the wellbore. However, within the Bakken Formation, field data suggest that operators are unable to sustain propped fractures spatially or temporally (2, 3), resulting in decreased oil production. The key goals of this project included the evaluation of formation integrity relative to exposure to various fracturing and reservoir fluids and the evaluation of proppant performance following exposure to fracturing and formation fluids at reservoir conditions.

Laboratory tests were conducted to evaluate the sensitivity of Bakken and Three Forks Formation cores to various fluids; evaluate the strength of Ottawa sand, an unspecified premium procured resin-coated sand (RCS), and ECONOPROP® lightweight ceramic proppant to various fluids; and measure the relative laboratory conductivity performance of propped fractures using actual rock core. Fluids used in experiments to examine potential strength degradation for both rock and proppant included slickwater – freshwater + polyacrylamide friction reducer; alkali

borate crosslinked water-based gel; gelled diesel; Bakken Formation crude; and Bakken Formation brine.

Fluid exposure tests were conducted by immersing the rock and proppant samples in each of the fluids in 250-mL glass sample containers. The containers were inserted into closed reactors and maintained at 250°F and 3000 psi for 30 days. Following exposure, tests were completed to examine rock and proppant strength relative to fluid exposure. Exposure studies helped to isolate circumstances that may contribute to a decrease in material strength over time.

Brinell hardness testing of formation core samples after exposure to fluids revealed that slickwater consistently decreased the hardness of the formation face for Middle Bakken Formation, Lower Bakken shale, and Three Forks Formation samples. The Middle Bakken samples appeared more susceptible to strength loss when exposed to fluids than did the other formation samples. Rocks exposed to gelled diesel experienced very little change in hardness.

Proppants exposed to Bakken Formation water (brine) consistently experienced the greatest increase in strain relative to proppants that were not exposed. The strength of RCS appeared to be affected detrimentally by all fluids and/or the high-temperature and pressure conditions of the reactor as compared to sand and ceramic. Fluids that had the greatest effect on RCS included crosslinked gel and Bakken oil and brine. Crush test results were consistent with elastic strength results of the various proppants and fluids, noting that resin-coated proppants do not normally produce a large quantity of crushed particles.

The results of this work demonstrated that the ceramic proppant was relatively unreactive and exhibited superior strength characteristics compared to the other proppant types following fluid exposures. RCS proppants are normally chosen to help prevent proppant flowback. However, these experiments suggest that fluid reactions and/or elevated temperatures and pressures with resin change the stress–strain relationship for RCS and that fluid considerations are important relative to the chosen resin.

The results of the conductivity testing demonstrated that at effective stress ranges of 6500–8000 psi, the ceramic proppant exhibited much higher conductivity than Ottawa sand (as much as 5 times greater) and moderately higher conductivity than RCS (as much as 2.3 times greater). However, this was using a solution of 2 wt% KCl. Given that the fluid exposure tests suggest the strength of RCS may be affected by reservoir conditions and fluid exposure and that slickwater and crosslinked gels have the potential to affect rock strength, advanced conductivity testing using the various fluids would be more representative of actual reservoir conditions.

Postmortem analysis of rock slabs used for the conductivity testing enabled evaluation of the mechanisms that may contribute to reduced conductivity, such as embedment or proppant crush. A Nanovea optical profiler was used to conduct a qualitative evaluation of embedment within the rock slabs. The results showed that between the different rock types, the Lower Bakken displayed the highest degree of embedment and spalling, followed by the Middle Bakken. The Three Forks slabs showed significantly less embedment than the Bakken rocks. Few patterns were apparent between proppant types, except that within the Lower and Middle Bakken, there appears to be a greater degree of ceramic proppant embedment than with the other two proppant types.

This is likely because of the higher strength of the ceramic proppant. Within the Bakken rock samples, the top slab of each pair showed deeper and wider embedment craters than did the bottom slab. This likely indicates an even distribution of proppants within the simulated fracture.

Overall, the results of this study indicate that fluid exposure may affect both rock and proppant strength and should be considered in the field. In addition, conductivity decreases within the Lower and Middle Bakken appear to be a function of a variety of factors, including proppant and rock strength as well as formation embedment and spalling. Formation embedment and spalling appear to be less significant within the Three Forks Formation. Ultimately, the results of this study highlight the need for conductivity testing using actual formation and/or fracturing fluids coupled with quantification of formation embedment and spalling. Given the importance of proppant performance on conductivity loss and, ultimately, oil recovery, better understanding the effects of these various factors on proppant and rock strength in the field is vital for more efficient production in unconventional oil and gas reservoirs.

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Subtask 1.9 – Demonstration of Gas-Powered Drilling Operations for Economically Challenged Wellhead Gas and Evaluation of Complementary Platforms

Program Area:	CRDP
Period of Performance:	9/1/11–3/31/13
Funding:	DOE: $400,000; Nonfederal: $703,125; Total: $1,103,125
EERC Subtask Manager:	Chad Wocken
DOE Technical Monitor:	William Fincham
Nonfederal Partners:	NDIC Oil and Gas Research Program
Final Report:	Dunham, G.E., Doll, T.E., and Wocken, C.A., 2013, Subtask 1.9 – demonstration of gas-powered drilling operations for economically challenged wellhead gas and evaluation of complementary platforms: Final report (September 1, 2011 – March 31, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2013-EERC-03-07, Grand Forks, North Dakota, Energy & Environmental Research Center, March.

The objective of Subtask 1.9 was to demonstrate and evaluate the use of wellhead gas to fuel diesel engines powering a drilling rig in North Dakota. The impetus for this study was the rapid growth of gas flaring in North Dakota, itself a function of rapid increase in oil production. This study comprised three major activities.

The first activity evaluated the operational limits of a 3512 Caterpillar diesel engine fueled simultaneously with natural gas and diesel. The gases studied included methane, a simulated Bakken Formation wellhead gas, and several heavier hydrocarbons ranging from C3 to C6, each tested separately with methane. The primary focus was to understand how heavier hydrocarbons, present at concentrations of up to 50% in Bakken gas, impact engine performance as measured by knock, cylinder pressure, and ignition delay. Testing was conducted over a range of diesel replacement ratios and load in order to establish the limits of acceptable engine performance. Understanding the performance limits will help protect engines against potential damage and improve the performance of fumigation-based Bi-Fuel® systems from Altronic, LLC. Further, data collected from these experiments could be used to establish operating conditions for subsequent field demonstrations on a drilling rig to ensure reliable engine operation, optimal fuel use, and economic benefit from reduced diesel fuel consumption. Results and conclusions from this activity are as follows:

- The work demonstrated that a diesel engine can operate in a Bi-Fuel mode with simulated Bakken Formation gas at replacement rates exceeding 40%. A properly installed and operating Bi-Fuel system can be used to supply Bakken Formation wellhead gas to a diesel engine while protecting the engine from knock.

- At low engine load and high replacement rates, unburned hydrocarbons were measured in the stack. To avoid this condition in field operations, the Bi-Fuel system is designed with instrumentation and a control system that monitor engine performance to ensure proper fuel combustion and smooth engine operation. When it is desirable to vary a diesel replacement rate as load varies, the STEPCON® (stepped control) can be used.

- At higher engine load, near 60%, engine knock occurred when Bakken gas was fumigated at 70% replacement rates, well above typical Bakken gas operating limits. The actual replacement rate based on diesel fuel consumption was approximately 40%. Under these conditions, unburned fuel was measured in the exhaust. The presence of some unburned hydrocarbon in the exhaust can be attributed to the normal engine aspiration cycle. However, some may also be attributed to the age of the engine and the relatively low compression ratio of 13/1.

- The ignition delay and peak cylinder pressure data collected during these tests are consistent with knock data and indicate that replacement of diesel fuel with a Bakken Formation gas is lower than can be achieved with high-methane pipeline gas.

- The components of Bakken Formation gas (C3–C6) individually with methane do not cause knock when blended at typical concentrations. However, when blended at high rates, the pentane and hexane caused engine knock. The individual limits appear to be around 2.5%–3.0%. The effect of the higher hydrocarbons is more than likely cumulative since knock was observed at high replacement rate with simulated Bakken gas in which the pentane and hexane concentrations were nominal. Results from the tests with the individual gases provide useful qualitative information but do not enable predictions on how mixed gases impact engine performance.

The second activity consisted of field-testing engines using a mixture of diesel and untreated wellhead gas, or bifuel, on a drilling rig during the drilling of two wells. A bifuel system operates by fumigating natural gas into the air intake of the diesel engine, reducing the amount of diesel fuel required to meet load. The bifuel system used for this project was provided by Altronic and is marketed as GTI Bi-Fuel. CLR along with its drilling contractor, Cyclone Drilling, provided access to a drilling rig for this demonstration project. Cyclone Rig No. 28 is powered by three 3512C Caterpillar diesel engines that were modified by ECO-Alternative Fuel Systems (ECO-AFS) with STEPCON Bi-Fuel systems, manufactured by Altronic.

The results of the 47-day demonstration of bifuel for rig power illustrated that using wellhead gas in bifuel applications to power a drilling rig can lead to an overall decrease in diesel fuel use, fuel cost, and truck transport of liquid fuel without adversely impacting drilling operations. Specific results included the following:

- Reduced diesel fuel use by 16,000–18,500 gal and associated fuel delivery truck traffic
- Fuel-related cost savings of nearly $60,000 because of the lower value of wellhead gas relative to diesel
- Beneficial use of wellhead gas at the point of production
- Decreased nitrogen oxide and increased carbon monoxide and nonmethane hydrocarbons when compared to diesel-only engine operation, which can be mitigated by adding catalytic emission control to the engine exhaust
- Seamless operation of the GTI Bi-Fuel system, with no impact on drilling operations
- Additional fuel savings possible by minimizing diesel-only operation with optimized process control and/or operational oversight of the GTI Bi-Fuel system
- Bifuel systems operated efficiently with routine engine maintenance

Although bifuel operation of drilling rigs is beginning to be recognized as a viable option for producers, the majority of drilling rigs in North Dakota are still fueled by diesel only. Logistical and contractual issues can complicate the availability of wellhead gas for drilling operations. However, the results from this study highlight the benefits of working through these issues and expanding implementation of bifuel systems. Based on the results of this activity, the project team estimated the overall effect of using otherwise flared wellhead gas to power drilling operations of nearly 200 drilling rigs in North Dakota. Such broad implementation would result in the following:

- 1,800,000 Mcf wellhead gas used to power drilling rigs in 1 year (2% of currently flared wellhead gas)
- 18,000,000 gal of diesel fuel saved in 1 year
- $72,000,000 diesel fuel costs saved in 1 year

- 3600 fuel truck deliveries (5000-gal tanker) avoided in 1 year

- Air emission reduction can be achieved using commercially available diesel engine exhaust gas treatment (catalytic conversion)

These technologies are capable of reducing CO and nonmethane hydrocarbon emissions in bifuel-operated engines to levels similar to 100% diesel-only operation.

The third major activity conducted under this project focused on examining technologies that can use the associated gas at locations upstream of traditional natural gas-processing plants, thereby extracting value from a currently uncaptured resource. Economic analysis of these technologies consisted of comparing capital expenses to potential revenue generation in an effort to frame the potential for more detailed economic study specific to individual technologies. Technologies evaluated included natural gas liquid (NGL) recovery, compressed natural gas (CNG) for vehicle fuel, electrical power generation, and chemical production.

Bakken associated gas is typically low in sulfur and high in NGLs, creating both unique challenges to use and economic opportunity since NGLs are currently more valuable than the dry natural gas. Deploying small-scale NGL recovery systems as an interim practice while gathering lines are built allows the highest value and most easily transported hydrocarbons to be marketed. Further, the leaner gas generated from these systems can be more easily used for power or transportation fuel or transported as a compressed gas. Clearly, NGL recovery would be most economical at wells flaring larger quantities of gas, immediately after production begins to capture the greatest volume of gas. Additionally, technology mobility is critical to enable relocation to new wells as gas-gathering infrastructure is constructed.

While there may be several other drivers to warrant the use of CNG in the Bakken region, economics alone will most likely not justify conversion of medium-sized fleets of vehicles to CNG if a distributed CNG refueling approach is taken. Bakken associated gas is too rich with NGLs and too variable in composition to be used as-is in natural gas vehicles (NGVs). It must be purified to a strict specification and compressed before being dispensed to a vehicle. Further, vehicle fleets using the CNG fuel would need to be adaptable and flexible to take advantage of this stranded and transient gas resource. In spite of these drawbacks, at the time of this study (2011–2012), U.S. Energy Information Administration (EIA) data indicated that CNG prices had been significantly lower and experienced less volatility over the course of a decade when compared to gasoline and diesel fuels and that the price gap was expected to continue through 2015.

The demand for power in the Williston Basin has grown rapidly. In addition to meeting this growing demand, utilities are also faced with ensuring grid reliability. Forecasts suggest a tripling of the electric load in oil-producing areas of western North Dakota and eastern Montana. An initial review of the characteristics of each distributed power generation technology eliminated some options from further consideration. Based on this review, three technologies were evaluated: reciprocating engine, gas turbine, and microturbine. When evaluating power generation scenarios, the projects were characterized into two distinct categories based on the primary use of the electricity: grid support and local power. In general, power production using rich associated gas is a viable option. A wide variety of power generation technologies exist that can, without much

difficulty, use rich gas of varying quality to produce electricity and are scaled to wellhead flow rates.

The petrochemical industry is dominated by large processing plants where economy of scale and access to large gas fields maximize profitability. Despite rapid and significant growth of gas production in North Dakota, only a small fraction of total U.S. natural gas is produced in the state. Pipeline and rail export of gas and NGLs to existing petrochemical infrastructure is likely to continue to be the predominant mode to market these resources. Although natural gas export is likely to dominate in North Dakota, opportunity exists for small-scale technologies that can convert low-cost gas to higher-value chemicals or fuels that have a strong regional demand. The production processes with the best opportunity for economic success at the well site include novel fertilizer production technologies or innovative gas-to-liquid approaches that can be scaled appropriately. All such processes would benefit by being mobile to periodically relocate to better-producing wells and avoid reduced use rates.

Although none of these approaches appear to be highly compelling from a purely economic standpoint, two end-use technologies were identified that represent technically feasible applications: CNG and power production. The high price of transportation fuel relative to CNG creates some advantages; however, rich gas cannot be used in standard NGVs because of concerns over emissions and engine performance. In the case of power production, these technologies match nicely the scale and temporal nature of the associated gas resource. In either case, small-scale NGL recovery, although less efficient than at large centralized facilities, may be an enabling technology, allowing value to be extracted from the associated gas while improving economical use of leaner gas for transportation and power. Chemicals production would be the most challenging to deploy at small scale in the Williston Basin, but some chemicals (specifically nitrogen-based fertilizers) may hold some promise.

The table below summarizes the end-use technologies evaluated and their characteristics as they relate to deployment in the Williston Basin.

Summary of Evaluated Technologies with Qualitative Characteristics

Technology	Gas Use Range, Mcfd	NGL Removal Requirement	Scalability to Resource	Ease of Mobility	Likelihood of Deployment at Small Scale
Power – Grid Support	1000–1800	Minimal	Very scalable	Very easy	Very likely
Power – Local Load	300–600	Minimal	Very scalable	Very easy	Very likely
CNG	50+	Yes	Scalable	Very easy	Possible
Chemicals	1,000,000*	No	Not scalable	Not mobile	Very unlikely
Fertilizer	300–2000	No	Scalable	Not easy	Possible
Gas-to-Liquids	1,000,000*	No	Scalable	Easy	Possible

*Typical commercial-scale plant.

Subtask 1.10 – CO_2 Storage and Enhanced Bakken Recovery Research Program

Program Area:	CS
Period of Performance:	5/1/12–11/30/13
Funding:	DOE: $675,000; Nonfederal: $802,069; Total: $1,477,069
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	Michael McMillian
Nonfederal Partners:	Continental Resources (CLR), Marathon Oil, NDIC, and TAQA North USA (TAQA)
Final Report:	Sorensen, J.A., Hawthorne, S.B., Smith, S.A., Braunberger, J.R., Liu, G., Klenner, R.C.L., Botnen, L.S., Steadman, E.N., Harju, J.A., and Doll, T.E., 2014, Subtask 1.10 – CO_2 Storage and Enhanced Bakken Recovery Research Program: Final report (May 1, 2012 – May 31, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2014-EERC-06-13, Grand Forks, North Dakota, Energy & Environmental Research Center, June.

The first phase of the CO_2 Storage and Enhanced Bakken Recovery Research Program was conducted under Subtask 1.10, which comprised laboratory and modeling activities to examine the potential for CO_2 storage and EOR in the Bakken. Total oil in place estimates for the Bakken petroleum system range from 160 Bbbl to over 900 Bbbl. Most estimates for primary recovery range from 3% to 6%, depending on reservoir characteristics. Therefore, small improvements in productivity could increase technically recoverable oil in the Bakken by billions of barrels. While the use of CO_2 in conventional reservoirs is a widely applied practice, its use for EOR in tight oil reservoirs is a relatively new concept. If successful, the large-scale injection of CO_2 into the Bakken will not only increase oil productivity but will also result in the geologic storage of significant amounts of CO_2.

Specific activities included the following:

- Characterization of rock samples from four different areas of the Bakken in North Dakota
- Creation of static geologic models for two of those areas, the Bailey and Grenora areas, and subsequent dynamic simulation modeling of possible CO_2 injection schemes to predict the potential CO_2 storage and EOR in those areas
- Laboratory studies to evaluate the ability of CO_2 to remove hydrocarbons from Bakken shales and Middle Member lithofacies
- Laboratory determination of MMPs for Bakken oil samples using an innovative technique
- Evaluation of data from a CO_2 injection test conducted in the Elm Coulee area of Montana in 2009 and the possible application of knowledge gained to future injection tests in other areas

- A first-order estimation of potential CO_2 storage capacity in the Bakken Formation in North Dakota

Key findings included the following:

- Initial estimates of CO_2 storage resource using the method for estimating geologic storage potential in oil and gas reservoirs, as outlined in the DOE Carbon Sequestration Atlas of the United States, suggest that the Bakken in North Dakota may have a CO_2 storage resource ranging from 121 Mt to 3.2 Gt. This broad range indicates that more data are required to develop more accurate assessments of CO_2 storage potential in tight oil-bearing formations such as the Bakken.

- Results of dynamic simulation modeling of the Bailey area in Dunn County suggest that the injection of CO_2 could increase oil production by as much as 50%. They also indicate that a scheme that pairs two injection wells with a single production well was the most effective approach for EOR of the schemes modeled.

- Laboratory experimental studies indicate that CO_2 can remove over 90% of hydrocarbons from Bakken reservoir rocks and up to 60% from the shales in a time frame that ranges from hours to days in small-scale elution experiments. Diffusion appears to be the primary mechanism driving the observed hydrocarbon removal.

- In the Bakken, CO_2 flow will be dominated by fracture flow and not significantly through the rock matrix. Fracture-dominated CO_2 flow could essentially eliminate the displacement mechanisms responsible for increased recovery in conventional reservoirs. As such, other mechanisms, such as diffusion, must be optimized in tight reservoirs.

- The Elm Coulee injection test appeared to result in a delayed improvement in oil production. The improved oil production was not seen until 6 months after the test, but it lasted for a few months.

- Simulation results indicated that diffusion may play a significant role in moving oil from the reservoir matrix into the fracture network.

- The concept that diffusion plays a significant role in CO_2 movement in the Bakken, as indicated in laboratory and modeling results, is also supported by the delayed improvement in oil production after the Burning Tree CO_2 injection test. This suggests that the role of diffusion in the behavior of CO_2 in the Bakken should be a subject for further research.

The results of these activities suggest that CO_2 may be effective in enhancing the productivity of oil from the Bakken and that the Bakken may hold the ability to geologically store significant amounts of CO_2. However, there are no clear-cut answers regarding the most effective approach for using CO_2 to improve oil productivity or the storage capacity of the Bakken. The results underscore the notion that an unconventional resource will likely require unconventional methods of both assessment and implementation when it comes to the injection of CO_2. With that

in mind, it is clear that additional knowledge is necessary to make informed decisions regarding the design and implementation of potential injection and production schemes. In particular, a better understanding of the fundamental mechanisms controlling the interactions between CO_2, oil, and other reservoir fluids in these unique formations is necessary to develop accurate assessments of potential CO_2 storage.

Another issue that must be addressed is that existing modeling and simulation software packages do not adequately address or incorporate the unique properties (e.g., microfractures, high organic carbon content, combined diffusion, adsorption, and darcy flow or the physical interactions between the injected CO_2 and formation fluids) of these tight, unconventional reservoirs in terms of their impact on CO_2 behavior. These knowledge gaps can be filled by conducting scaled-up laboratory activities integrated with improved modeling and simulation techniques, the results of which will provide a robust foundation for pilot-scale field injection tests. Finally, field-based data on injection, fluid production, and long-term monitoring from pilot-scale CO_2 injection tests in the Bakken are necessary to verify and validate the findings of the laboratory- and modeling-based research efforts. The work of the CO_2 Storage and Enhanced Bakken Recovery Research Program continued under Subtask 2.20.

Task 2.0 – Climate Change and CO_2 Sequestration

Subtask 2.1 – Assessment of the Feasibility of Geothermal Generation at CO_2 Geosequestration Sites

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $30,000; Nonfederal: NA; Total: $30,000
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	Paula Flenory
Nonfederal Partners:	NA
Final Report:	Dobroskok, A.A., Sorensen, J.A., Holubnyak, Y.I., and Harju, J.A., 2009, Subtask 2.1 – assessment of the feasibility of geothermal generation at CO_2 geosequestration sites: Final report (July 1, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2009-EERC-05-08, Grand Forks, North Dakota, Energy & Environmental Research Center, May.

The objective of Subtask 2.1 was to develop a method to aid in the assessment of the benefits of geothermal generation for a CO_2 storage project. Development and use of renewable energy resources are priorities for many government agencies and commercial entities worldwide. Geothermal energy offers the capability to provide continuous baseload power, near-zero emissions, and the success of ongoing geothermal generating projects worldwide. However, its feasibility comes into question for operations involving production of hot water from subsurface reservoirs such as coproduction of water in the oil and gas industry and CO_2 sequestration. Production of water in a CO_2 storage operation is not a necessity, but it can provide the benefit of

relieving pressure build-up in the target formation due to CO_2 injection and potentially help offset some of the costs involved in powering the operations.

The EERC aimed to create a computerized tool for the assessment of the feasibility of geothermal generation at CO_2 sequestration sites. Thus the method uses a set of parameters that are readily available in the initial stages of project planning or are easy to access. Input data are the best available estimates, and using detailed numerical models describing the system is not likely to provide significant improvement over the estimates provided by simpler models. Therefore, the method developed is based on the relatively simple models applicable to the processes considered. The method was designed for the present-day state of geothermal generation technology and uses data collected in ongoing geothermal projects and studies conducted by others. The available data were collated and summarized into databases. When feasible, empirical relationships were derived for the simplification of analysis.

The feasibility of geothermal generation was understood as commercial feasibility of the operations. Components believed to influence commercial feasibility of a project include economic parameters, component costs, resource, environmental and safety issues, and costs involved in using conventional energy sources. The method created accounted for each of those components, and the computer code developed includes the modules corresponding to the following features of a geothermal project:

- CO_2 flow in the injection well
- CO_2–water flow in the subsurface reservoir
- Heat transmission in the reservoir
- Water flow in the production well
- Power output
- Capital and operational costs (including costs of mitigating environmental effects)

The results of the study indicated that only high-grade sources would likely provide viable options for geothermal generation. The grade of a source is defined by the formation temperature and pay thickness. In particular, the case study conducted for the Fort Nelson CO_2 Capture and Sequestration Project showed that geothermal generation would not be feasible at the site.

Subtask 2.2 – Creating a Numerical Technique for Microseismic Data Inversion

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $90,000; Nonfederal: NA; Total: $90,000
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	Steven Markovich
Nonfederal Partners:	NA
Final Report:	Dobroskok, A.A., Holubnyak, Y.I., and Sorensen, J.A., 2009, Subtask 2.2 – creating a numerical technique for microseismic data inversion: Final report (March 30, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2009-EERC-05-04, Grand Forks, North Dakota, Energy & Environmental Research Center, May.

The objective of Subtask 2.2 was to develop a technique for the inversion of passive seismic data recorded during hydraulic fracture propagation in an effort to unify passive seismic monitoring and numerical modeling. Joining geomechanical and geophysical monitoring is an important direction in geoengineering and has stimulated the development of appropriate theoretical and numerical techniques for decades. The techniques allow geomechanical and geophysical approaches to complement each other by eliminating the shortcomings and unifying the advantages. The development of the techniques has resulted in the creation of the basis that will allow for the unification. The next step is the application of the multidisciplinary approach developed to the specific problems of geotechnical engineering. One of the most important geotechnical problems is the characterization of the subsurface system and understanding the processes taking place in the system, which is complicated by the complexity and the limited access to the system.

Of the variety of geophysical techniques employed in the attempt to resolve the problem, one of the most promising is passive seismic monitoring. The essence of the technique is recording the acoustic signals produced in the subsurface either naturally or in response to human activity. The acoustic signals are produced by mechanical displacements on the contacts of structural elements (e.g., faults, boundaries of rock blocks, natural and induced fractures). The process can be modeled by modern numerical techniques developed in geomechanics. This project was aimed at the unification of passive seismic monitoring and numerical modeling. In particular, the unification targeted development of a technique for the inversion of passive seismic data recorded during hydraulic fracture propagation.

The approach adopted in the study consisted of numerical modeling of the seismicity accompanying hydraulic fracture propagation and defining seismic attributes and patterns characterizing the process and fracture parameters. Numerical experiments indicated that the spatial distribution of seismic events is correlated to geometrical parameters of hydrofracture. Namely, the highest density of the events is observed along the fracture contour, and projection of the events to the fracture plane makes this effect most pronounced. Thus determining the plane with the best-defined grouping of the events helps in finding the fracture plane. The numerical

experiments also showed that dividing the totality of the events into groups corresponding to the steps of fracture propagation allows for reconstructing the geometry of the resulting fracture more accurately than it has been done in the majority of commercial applications.

These features provide the basis of the method for inversion of microseismic data. In particular, a strip ray scanning (SRS) technique for data interpretation was compared to the principal component analysis (PCA) technique suggested by other authors. It appears that when applied to the totality of seismic events, both methods are capable of catching the fracture plane with reasonable accuracy. Still, the totality of event locations, even projected to this best-fit plane, does not provide unambiguous estimation of the fracture sizes. To find the latter, it is better to use statistically significant groups of events occurring on time steps. Application of PCA and SRS to these groups tends to delineate the fracture front and the direction of the front propagation in time.

This study concluded that the PCA and SRS methods may complement each other when analyzing the totality of the events, while the SRS method appears to be a proper tool to trace the fracture front on time steps and the length of a fracture. Both techniques were implemented into a computer code, which was used for the analysis of acoustic emission data recorded in laboratory experiments and miscroseismic data from mines and allowed to reasonably reconstruct the geometry of the mine and the fracture created in physical experiments. The technique has a potential to be extended for the case of hydrofracture branching and characterizing fluid paths in subsurface reservoirs.

Subtask 2.3 – Geological CO_2 Sequestration with Methane Farming

Program Area:	CRD
Period of Performance:	7/1/08–11/30/09
Funding:	DOE: $100,000; Nonfederal: NA; Total: $100,000
EERC Subtask Manager:	Dingyi Ye
DOE Technical Monitor:	William O'Dowd
Nonfederal Partners:	NA
Final Report:	Ye, D.; Schmidt, D.D. *Subtask 2.3 – Geological CO_2 Sequestration with Methane Farming*; Final Report (June 25, 2008 – Nov 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-11-08; Energy & Environmental Research Center: Grand Forks, ND, Nov 2009.

Subtask 2.3 involved an investigation of a biotechnology to convert unminable coal and residual oil to methane as well as to improve geologic CO_2 sequestration technology by coupling it with methane "farming." The objectives of the project were to:

- Conduct bench-scale experiments to prove the hypothesis that, under suitable conditions, methane can be produced from unminable coal and the residual oil sampled from the coal seam and oil well that is currently used for geologic CO_2 sequestration testing.

- Determine the optimal nutrient conditions for farming methane.

- Continue and complete an on-site column experiment started in 2007 under a separate project.

Laboratory study provided data to support the hypothesis that methane can be produced from unminable coal and crude oil. Tests were conducted with crude oil, formation water, and coal samples collected from two sites in North Dakota. Initial experiments showed methane formation in the oil–water (crude oil plus formation water) culture when methanogenic substrates were provided. Detection of the methane in the oil–water culture confirmed the presence of methanogenic bacteria in the oil–water sample. The cultures of the initial experiment were then transferred. Beginning on Day 11, methane production was detected in two coal-containing groups with and without addition of the methanogenic substrates. These results proved that methanogens were also present in the coal samples.

Further laboratory experiments were conducted to clarify whether the observed methane production was from coal or yeast extract. While methane formation was also observed in the coal culture that did not receive methanogenic substrates, since this culture also contained yeast extract (2.5 g/L) and yeast extract has ~38% organic carbon, it was unclear whether the methane was converted from the coal components or yeast extract. To clarify this, further experiments were set up to transfer the culture into three types of subcultures—with yeast extract, without yeast extract, and without yeast extract but with vitamins. Methane was formed in the subculture containing yeast extract; however, after 12 weeks of incubation, no methane was detected in the subcultures without yeast extract regardless of whether the vitamins were added or not. These results suggest that the CH_4 was probably produced from the yeast extract, not the coal components.

Another experiment was set up to determine carbon and energy sources that support the methanogenic activities for the oil and coal samples. The results showed that acetate and methanol did not support the methanogenic activities in either oil or coal samples. H_2/CO_2 supported the methanogenic activity in both oil and coal samples, whereas formate supported methanogenic activity in the oil sample. The different carbon/energy preference reflects the difference in the methanogenic population in the two samples.

Nutrient requirements were determined with the coal-containing cultures. The results indicated that under our experimental conditions, methanogenic carbon and energy sources were the major limiting factor for the methanogenic activity. When the substrate requirements were satisfied, nutrients among Ca, Mg, Fe, and S (one or more than one) became the activity-limiting factor. Integration of these results suggests that even though methanogens in the coal samples are enriched, more samples are required to screen for active anaerobic coal-degrading microorganisms.

In the absence of external carbon, a trace amount of methane was detected in the oil–water culture. This activity was maintained in the lab for further investigation. Experimental results confirmed the presence of methanogens for coal- and oil-sampling sites under geologic CO_2 sequestration testing and thus proved their potential for methane farming.

One of the goals of Subtask 2.3 was to continue and complete an on-site column experiment started in 2007 under another project. In the first phase of the project, a laboratory microcosm

study was conducted to investigate the effects of wetland restoration on microbial cycling of CO_2, CH_4, and N_2O in the glaciated North American prairie ecosystem, which included the laboratory experiments. The laboratory experiments eliminated impacts of some environmental variables (e.g., temperature, water content, plant cover, etc.) on microbial production and consumption of CO_2, CH_4, and N_2O, and the results may provide some information that might give an insight into the mechanisms regarding the effects of wetland restoration on microbial CO_2, CH_4, and N_2O cycling. However, laboratory conditions are different from in situ conditions, and results of the laboratory study cannot be directly extrapolated to field evaluation and prediction. In order to accurately quantitate the real effects of wetland restoration on field microbial CO_2, CH_4, and N_2O cycling, it was necessary to initiate an in situ microcosm study so that a high level of accuracy in evaluating and predicting effects of wetland restoration on carbon sequestration and GHG mitigation could be obtained.

The first phase of this activity primarily focused on verifying the effects and elucidating the possible mechanisms, while the second phase, reported here, focused on evaluating the real effects in situ. The goal of this phase was to explore a method to accurately estimate and predict changes in the CO_2, N_2O, and CH_4 budget by wetland restoration in the Prairie Pothole Region (PPR). The work comprised two on-site column experiments to quantitate changes in CO_2, N_2O, and CH_4 fluxes from the investigated wetlands in the PPR "before" and "after" wetland restoration and examine effects of N-fertilizers on CO_2, N_2O, and CH_4 emission from terrestrial ecosystems.

Results of this in situ microcosm study showed that restoration of the wetland site would significantly reduce CO_2 flux. N-fertilizer enhanced the CO_2, N_2O, and CH_4 emissions and linearly correlated to the CO_2 flux within the experimental rate range (46–200 kg N ha^{-1}). The experimental results also clarified that the overall reduction in global warming potential (GWP) by wetland restoration was mainly contributed from CO_2 sequestration. These results demonstrate that restoration of currently farmed wetlands in the PPR will significantly reduce the GWP budget.

Subtask 2.4 – Integration and Synthesis in Climate Change Predictive Modeling

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $50,000; Nonfederal: NA; Total: $50,000
EERC Subtask Manager:	Jarda Solc
DOE Technical Monitor:	Ron Breault
Nonfederal Partners:	NA
Final Report:	Solc, J., 2009, Subtask 2.4 – integration and synthesis in climate change predictive modeling: Final report (March 30, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2009-EERC-06-06, Grand Forks, North Dakota, Energy & Environmental Research Center, June.

In Subtask 2.4, the status of predictive modeling was evaluated to assess options and the feasibility of integrating previous paleohydrologic reconstructions and their synthesis with global climate scenarios. Models applied in the field of climate modeling include coupled atmosphere–

ocean general circulation models and earth system models of intermediate complexity. While both models are capable of providing quantitative estimates at continental and larger scales, their application on a regional scale is limited.

The climate models evaluated were the Atmosphere–Ocean Global Circulation Model (AOGCM) and Earth System Models of Intermediate Complexity (EMICs). While both models are capable of providing quantitative estimates at continental and larger scales, their application on a regional scale is limited.

Results of EERC research indicated that short-term data series available from modern instrumental records are not sufficient to reconstruct past hydrologic events or predict future ones because the instrumental data represent only fractions of climate cycles. Reconstruction of paleoclimate phenomena provided credible information on past climate cycles and confirmed their integration in the context of regional climate history is possible. The paleoclimate proxies from the northern Great Plains may be more representative of the global climate cycles because of their unique position on a transboundary between three climatic provinces—Atlantic, Pacific, and Arctic. Similarly to ice cores and other paleo proxies, acquired data represent a credible tool for model calibration and validation of observed trends. It remains a subject of future research whether further refinement of the results and synthesis with regional and global climate observations could lead to credible climate predictions on a regional scale.

Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II

Program Area:	SNESS and CC
Period of Performance:	7/1/08–4/30/13
Funding:	DOE: $1,929,679; Nonfederal: $890,625; Total: $2,820,304
EERC Subtask Manager:	Brandon Pavlish
DOE Technical Monitor:	Arun Bose
Nonfederal Partners:	Arthur J. Gallagher, ATCO Power, Baker Hughes, Black & Veatch, Cansolv Technologies, CO_2 Capture Project Consortium (BP, Chevron, Eni, BR Petrobas, Shell, and Suncor), Constellation Power Source Generation, C-Quest Technologies, GE Global Research, Hitachi, Huntsman Petrochemical, Ion Engineering, Metso Power, Midwest Generation, Minnesota Power, Nebraska Public Power District (NPPD), NDIC, PPL Montana (Puget Sound Energy, Portland General Electric, Avista, and PacificCorp), Saskatchewan Power (SaskPower), Sulzer, and TransAlta Utilities
Final Report:	Pavlish, B.M.; Kay, J.P.; Laumb, J.D.; Strege, J.R.; Fiala, N.J.; Stanislowski, J.J.; Snyder, A.C. *Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II*; Final Report (Sept 1, 2010 – April 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-08-17; Energy & Environmental Research Center: Grand Forks, ND, Aug 2013.

To address the challenge of applying CO_2 capture to coal-fired utilities, the multiphase, multiyear, multipartner PCO_2C Program was initiated under Subtask 2.5. Development of an economically viable CO_2 capture technology presents one of the biggest challenges to the fossil energy industry in the 21st century. Many existing technologies are capable of capturing CO_2 from coal-fired power plants, but none have been applied at a commercial scale, and most are likely to be inefficient and expensive when applied to these facilities. During Phase I of the PCO_2C Program, two state-of-the-art carbon capture systems were designed and fabricated for use in multiple applications. Phase II of the program featured testing that used Phase I results to advance the most promising technologies toward commercialization and to evaluate novel approaches that may not be commercialized as quickly but have the potential for significant cost savings.

Throughout Phases I and II, several activities were completed that covered a wide range of technology evaluations. The goal of this program was to evaluate technologies to determine the most promising options to move forward, either through continued testing and evaluation at the pilot scale or perhaps in a larger-scale demonstration activity. The focus was to examine technologies that could be commercially deployed in the next 5 to 10 years. The PCO_2C Program successfully designed and implemented a flexible CO_2 capture system to test a variety of technologies that are currently in the development stage. CO_2 capture technologies that are under development involve the use of an absorption column for gas–liquid contacting and a stripper (or regenerator) column to regenerate the spent solvent and produce an almost pure stream of CO_2 ready to be dehydrated and compressed. A portable system was designed and constructed to be operated with pilot-scale combustion equipment at the EERC and as a slipstream for larger-scale testing. Input from project sponsors was solicited during the design phases. The physical system was changed during the course of the project, including adding a second absorption column, to continue to improve the quality of the data it produced.

In Phase I, one of the EERC's existing pilot-scale combustion units was retrofitted with a portable, flexible absorption and stripping system in order to evaluate advanced and novel solvents under development. Hitachi's H3-1 and methyldiethanolamine (MDEA) plus piperazine (PZ) were tested for their ability to absorb CO_2 from subbituminous coal-derived flue gas. The results were compared against a baseline case of 30 wt% MEA. At least 90% capture was achieved for all three solvents at similar test conditions. The results indicated that the two advanced solvents required 10% to 35% less energy than MEA and that less solvent was needed to achieve the same capture rates. Corrosion of process equipment was also monitored during the testing by analyzing the samples for trace metals. In general, corrosion product concentrations were very low; longer-term testing is needed to draw conclusions on specific solvent corrosion rates.

One of the EERC's existing pilot-scale combustion systems was retrofitted to permit oxygen firing. Several weeks of oxygen-fired testing was performed using four different coals to determine the effect of coal rank with the changing combustion atmosphere. This testing showed that preventing air from leaking into the system is the main challenge for retrofitting an existing coal-fired combustion system into an oxygen-fired system. Other challenges included meeting the CO_2 purity required for EOR without significant postprocessing cleanup.

A value-added report was generated to address water use and recovery as nearly complete water removal is necessary before a CO_2 stream can be transported by pipeline to a storage target.

A LDDS was built and tested during both the oxy-fired and postcombustion tests. The calculated cost of the moisture recovered was about 10 times that of conventionally treated sources, meaning that novel integration strategies would be needed to make the LDDS concept more attractive.

Aspen Plus® was used to model the Phase I test data for both the oxy-fired and advanced solvent systems for a 500-MW power plant. The cost of CO_2 capture using an oxygen-fired retrofit was found to be US$42/ton. The capture cost was reduced to US$34/ton in the best-case scenario of an advanced solvent in a highly efficient power plant.

In Phase II, pilot-scale testing was conducted using advanced solvents provided by Hitachi, Huntsman, Cansolv Technologies, and ION Engineering and their performance compared to that of MEA. Both coal-based and simulated natural gas combined-cycle (NGCC)-based flue gases were employed during the testing. Aspen modeling software was used to evaluate the economics of each solvent. Additional work evaluated the CO_2-scrubbing efficiency of the DOE National Energy Technology Laboratory (NETL) immobilized amine solid sorbent.

One week of oxygen-fired testing focused on the emission of HAPs, including HCl, mercury, and SO_3. Results showed that recycling flue gas to the boiler generated a smaller flue gas stream but that it contained HAPs at higher concentrations than that of air-blown combustion. However, because the total volume of gas emitted is decreased, fewer emissions are produced.

Phase II results for testing conducted with coal concluded that significant CO_2 capture savings are achievable, with CO_2 capture costs being reduced from the DOE MEA Base Case 10 from US$45/ton to as low as US$27/ton for the advanced solvents tested. This cost yields an increase in the cost of electricity of 37%, which is only slightly higher than DOE's target of 35%. Based on these results, a slipstream project has been planned to evaluate the most promising option at a 0.5–1.0-MW_e scale, a 5- to 10-fold scale-up of the technology. Several host sites have expressed interest, and the final details are currently being worked out for this effort.

All of the solvents studied in Phase II were tested in a system with a single absorption column and a single stripper column for both coal-derived and NGCC flue gas testing. After all testing was complete and the data were reduced, it was discovered that the regeneration energy required for MEA was exceptionally high under NGCC flue gas. Examination of the solvent loading revealed that although the lean solvent exiting the stripper was quite lean, the rich solvent exiting the absorber was also very lean when operating with simulated NGCC flue gas. This implied that the absorption column, which had been designed for coal-derived flue gas, was too short and that there was not enough contact time to achieve good capture with the low CO_2 concentrations present in simulated NGCC gas.

A second absorption column was built, and two of the solvents, MEA and ION, were then retested with the added residence time under NGCC flue gas. The regeneration energy for MEA was greatly reduced with the addition of a second column. The ION solvent also performed more similarly to what was expected from testing with coal-derived flue gas.

Based on current results, it is clear that a range of advancements has been shown over that of MEA for NGCC conditions. The results show a cost range of US$36 to US$41/ton of CO_2

captured (not avoided costs). Although these cost projections are for a generic plant case, the overall trends should be similar on a specific plant analysis. Several other factors will need to be considered when these technologies are examined as a retrofit option, which could result in significant increases to the projected costs shown here.

Overall, corrosion product concentrations were very low for all solvents, and long-term testing would be needed to make firm conclusions on specific solvent corrosion rates. Solvent samples from Phase I test runs were analyzed for corrosion and degradation product concentrations. MEA had the highest amounts of sulfate and thiosulfate, followed by H3-1; Huntsman additive had the least amount of these salts. The main organic salts found in the samples were formate, acetate, and oxalate, which are oxidative degradation products of amine-based solvents. Organic ion concentration was higher in MEA samples than Huntsman additive. H3-1 samples did not indicate any organic ions present. Solvents showing higher concentrations of degradation products would need a larger makeup stream when scaled up. Huntsman additive and H3-1 both represent potential cost savings over MEA in total solvent needs.

A value-added report was generated to provide a technoeconomic evaluation of the C-Quest CO_2 capture technology. Data from previous work conducted outside of the PCO_2C Program were used for the evaluation. Previous testing results indicated that the sorbent could be used to remove CO_2, and initial rates exceeded 80%. The economics of the solid sorbent system compared very favorably to traditional CO_2 capture systems. For comparison, an MEA solvent-based CO_2 capture system had a cost of US$46 per ton of CO_2 captured and an estimated electricity rate increase of US$0.058/kWh. The cost to purchase and transport the solid sorbent to the plant was shown to have a significant impact on the economics of the capture system.

Additionally, several other value-added reports were generated to explore life cycle assessments of amine, integration and implementation of CO_2 capture at existing coal-fired plants, and the emission challenges of amine use. Phase III of the PCO_2C Program was conducted under Subtask 2.18.

Subtask 2.6 – Assessment of Alternative Fuels on CO_2 Production

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $40,000; Nonfederal: NA; Total: $40,000
EERC Subtask Manager:	Debra Pflughoeft-Hassett
DOE Technical Monitor:	Steven Seachman
Nonfederal Partners:	NA
Final Report:	Pflughoeft-Hassett; Naasz, D.E. *Subtask 2.6 – Assessment of Alternative Fuels on CO_2 Product*; Final Report (June 25, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-06-13; Energy & Environmental Research Center: Grand Forks, ND, June 2009.

The impact of alternative fuels on CO_2 production and other emissions was assessed in Subtask 2.6. Many coal-based electric generating units (EGUs) use alternative fuels such as tire-derived fuel, waste biomass, used oil, and other recovered materials. The advantages of using these fuels include the recovery of energy from otherwise potentially wasted materials and the potential to reduce CO_2 and other emissions. To assess the impact of alternative fuels on CO_2 production and other emissions, the EERC performed the following activities:

- Assembly of information on the types and volumes of supplementary fuels used by U.S. coal-fired electric generators.

- Assembly of information on the units and boiler types where supplementary fuels are used.

- Determination of the CO_2 production, SO_2, and NO_x associated with alternative fuel use at coal-based electric generating facilities.

- Development of a carbon footprint associated with biomass use at a small electric generating facility.

- Assessment of the impacts to supplementary fuel usage if electric generators are subjected to more stringent emission regulation under Clean Air Act (CAA) Section 129, developed for solid waste incinerators (1).

DOE EIA 860 and 767 (2, 3) databases with alternative fuel use information for 2004 and 2005 were accessed and reviewed to determine what information on alternative fuels, combustion configuration, and emission controls was available from these resources. Alternative fuels were categorized by alternative fuel type, number of facilities using each fuel type, and heating value of solid, liquid, and gaseous alternative fuels.

The emissions associated with alternative fuels were evaluated, including SO_2, NO_x, and CO_2 emissions and compared with emissions from primary fuels. Biomass-based alternative fuels are considered to exhibit a net-zero CO_2 emission, while all other fuels emit some CO_2. CO_2 emissions are also associated with the transport of all fuels. A calculation of CO_2 emissions associated with the transport of biomass-based fuels that are typically accessed on a regional basis was made. Because the distance for transport of biomass-based alternative fuels was expected to be relatively short, the CO_2 emissions associated with transport of biomass-based fuels was expected to be lower than some other primary or alternative fuels transported using the same mode of transport.

A review of CAA emission regulations for coal-based electric generating facilities from Section 112 (4) and Section 129 (1) for solid waste incinerators was performed. Increased emission controls would be expected to be required if coal-based electric generating facilities using alternative fuels would be recategorized under CAA Section 129 (1) for solid waste incinerators, and if this change were made, it is anticipated that coal-fired electric generating facilities might reduce the use of alternative fuels.

Based on the assessment performed, the following conclusions were drawn:

- Alternative fuels are used broadly by coal-based electric generating facilities across the United States.

- Data imply that many alternative fuels are "opportunity fuels," and their use is based more on availability than on economic or environmental factors.

- Solid alternative fuels, with the exceptions of petroleum coke and waste coal, result in reduced SO_2, NO_x, and CO_2 emissions on a Btu basis as compared to coal.

- Biomass-based alternative fuels are considered carbon neutral but also are expected to have a smaller carbon footprint related to transport compared to other primary and alternative fuels.

- Changes in CAA emission regulation for coal-based electric generating facilities from Section 112 (4) to Section 129 (1) for solid waste incinerators should take into account the advantages of reduced emissions when alternative fuels are used to replace a percentage of fuel at coal-based EGUs.

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Subtask 2.7 – Transport Reactor for CO_2 Reduction in Lignite Coal and Subbituminous Coals

Program Area:	CRD
Period of Performance:	7/1/08–3/31/10
Funding:	DOE: $120,000; Nonfederal: NA; Total: $120,000
EERC Subtask Manager:	Scott Tolbert
DOE Technical Monitor:	Steven Seachman
Nonfederal Partners:	NA
Final Report:	Tolbert, S.G. *Subtask 2.7 – Transport Reactor for CO_2 Reduction in Lignite Coal and Subbituminous Coals*; Final Report (June 25, 2008 – March 31, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-03-06; Energy & Environmental Research Center: Grand Forks, ND, March 2010.

In Subtask 2.7, a study was performed to determine the flue gas CO_2 reduction effectiveness of solid adsorbents through the use of a recirculating transport reactor. Solid adsorbent materials are an emerging technology in the area of CO_2 capture that have shown initial promise over liquid solvents. This project focused primarily on the design, construction, and testing of a transport reactor for use in evaluating MEA- and diethanolamine (DEA)-based solid adsorbents and their ability to capture and release CO_2 from a coal-derived flue gas. The system was designed to use a slipstream from the EERC's CTF, which has, at its core, a 160-kW (550,000 Btu/hr) pulverized coal pilot plant test furnace that was originally constructed to study fouling and slagging properties of coals of all types and ranks. The CTF is also capable of burning natural gas, oils, biomass, municipal solid waste, and municipal sludge. Flue gas generated by the CTF may be passed through the SCR reactor, spray dryer, ESP, baghouse, cyclones, WFGD unit, and/or water capture system.

Typically, 150°C (300°F) is regarded as the boundary between low- and high-temperature CO_2 capture technologies for solid adsorbents. MEA- and DEA-based adsorbents were targeted because of the favorable energy balance of operating in the low-temperature range. Fixed-/packed-bed, moving-bed, fluidized-bed, and transport reactor designs were examined for use with these adsorbents. MEA- and DEA-based adsorbents exhibit an exothermic reaction in the presence of CO_2. Fixed-/packed-bed reactors used in testing small quantities of adsorbent have demonstrated thermal management problems resulting in polymerization of the adsorbent. Moving-bed reactors are prone to localized stagnation points that can lead to poor thermal management within the reactor, resulting in polymerization and agglomeration of the adsorbent. The careful design of a fluidized-bed reactor around media size and density is critical. To a lesser degree, fluidized-bed reactors may also exhibit localized stagnation points and agglomeration.

The intent of this project was to design a flexible and easily reconfigurable reactor to handle a wide range of media properties. Since reaction kinetics and physical properties among the adsorbents appear to be highly variable, a transport reactor was selected as the most applicable design for a solid–gas contactor. Adsorption versus desorption parameters of adsorbents are also widely varying. For this reason, it was determined that a single-loop reactor would be used to absorb CO_2 from flue gas, taken off-line and run in desorption mode, and then returned to adsorption mode. The transport reactor design can also be used as a fluidized-bed reactor.

Connection of the transport reactor to the CTF is normally downstream from the WFGD unit since the adsorbents have a sensitivity to sulfur, the temperature range is appropriate, and the flue gas is nearly saturated with water. Alternately, if drier gas is required, the transport reactor may be connected downstream of the water capture system. If the transport reactor was modified for use in the high-temperature range, it could be connected nearly anywhere in the CTF's system.

The transport reactor is constructed of 304 and 316 stainless steel (SS) since MEA and DEA degrade plastics and can cause corrosion of conventional steels. Although the transport reactor has a maximum operating temperature of 150°C, the temperature could be increased with minor modifications because of the reactor's SS construction. The reactor has heating and cooling capability to conduct both adsorption and desorption tests.

A positive displacement boost pump with a variable-speed motor is used to move flue gas through the system in a metered fashion. Adsorbent is recirculated and added to the system through the use of two augers. Since a wide variety of physical and chemical properties are targeted in this design, it was determined that augers would be used instead of J-legs. Each auger is driven by a variable-speed motor to control recirculation and addition rates. Adsorbent-to-flue gas volumetric ratios are maintained through the augmentation of the augers and boost pump. A cyclone is used for primary separation of solids. The cyclone is designed to be interchangeable to accommodate for varying adsorbent properties. A baghouse with back-pulse capability is located downstream of the cyclone to capture small or attritted particles not being recycled back through the reactor. Numerous pressure transmitters and thermocouples have been placed in the system to monitor the process. A hygrometer is located downstream of the baghouse to monitor humidity. Flue gas composition, upstream and downstream of the transport reactor, is monitored through the use of the CTF's gas analyzers. All motors, temperatures, pressures, heaters, cooling coils, and humidity are monitored and controlled through a data acquisition and control (DAC) system. The human–machine interface is facilitated by a touch screen display. The DAC system is highly reconfigurable and expandable.

The transport reactor is capable of handling particle sizes from 200 to 3500 µm (0.007 to 0.138 in.) with a minimum density of 300 kg/m^3 (18.7 lb/ft^3). The maximum initial volumetric charge is 56.5 L (2 ft^3) of adsorbent. Additional material may be added to the unit as material attrits or be drained off. The design fluidization velocity range is from 0.5 to 1.5 m/s (1.5 to 5 ft/s), although the boost pump is capable of velocities outside that range. Design residence times are approximately 2.2 to 6.7 s. The residence time range can be increased or decreased through modifications to riser length and/or diameter and/or changes in flue gas volumetric flow rate. The maximum pressure of the system is 101 kPa (gauge) (14.7 psig) but is operated under slight negative pressures normally used with the CTF.

Because of the development stage of the MEA/DEA solid adsorbent technology and the proprietary nature of the principal companies developing these adsorbents, the acquisition of adsorbent samples has been problematic, which has negatively impacted testing of true CO_2 adsorbents. As a result, the transport reactor has been functionally tested and validated with AC and other materials.

Subtask 2.8 – Development of Storage Coefficients for Carbon Dioxide Storage in Deep Saline Formations

Program Area:	CRD
Period of Performance:	8/25/08–7/31/09
Funding:	DOE: $32,679; Nonfederal: $60,716; Total: $93,395
EERC Subtask Manager:	Edward Steadman
DOE Technical Monitor:	Dawn Deel
Nonfederal Partners:	NA
Final Report:	Gorecki, C.D., Sorensen, J.A., Bremer, J.M., Ayash, S.C., Knudsen, D.J., Holubnyak, Y.I., Smith, S.A., Steadman, E.N., and Harju, J.A., 2009, Subtask 2.8 – development of storage coefficients for carbon dioxide storage in deep saline formations: Final report (August 25, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2009-EERC-07-06, Grand Forks, North Dakota, Energy & Environmental Research Center, July.

Subtask 2.8 comprised an investigation of storage resource/capacity and storage coefficients for CO_2 storage in DSFs. Storage resource/capacity estimates are critical for stakeholders to make informed decisions regarding the potential implementation of large-scale CO_2 storage. Previous methods based solely on fundamental geologic data grossly overestimate the storage resource/capacity of a given area, and for this reason, the concept of storage efficiency was introduced. One approach to developing more realistic estimates of storage resource/capacity is to use knowledge about a wider variety of physical properties of a rock formation as the basis for an assumption that only a certain percentage of that rock formation will be amenable to CO_2 storage. The value of that percentage is referred to as a "storage coefficient." The development of technically robust storage coefficients is critical to the advancement of broadly applicable and comparable storage resource/capacity estimates at all scales.

With this in mind, activities were conducted to 1) identify and evaluate previously developed methods for calculating storage resource/capacity, with an emphasis on those presented by the Carbon Sequestration Leadership Forum (CSLF) and DOE and then 2) develop a method and set of storage coefficients that could be applied to DSFs in a variety of settings at both the site-specific and formation scales. The primary objective of the work was to allow decision makers, scientists, and engineers to use the equations and concepts necessary to move estimates forward from "theoretical" to "effective" storage resources, thereby providing a more realistic view of the CO_2 resource/capacity of a given assessment area.

The two most promising types of storage formations for CCS are depleted hydrocarbon reservoirs and DSFs. Depleted hydrocarbon reservoirs are, for the most part, portions of saline formations that have proven trapping mechanisms and competent sealing units made apparent by the accumulation of hydrocarbons which have remained in place for millions of years. In addition, as a result of exploration and production activities, most depleted hydrocarbon reservoirs have a higher degree of characterization than DSFs. As a result, depleted hydrocarbon reservoirs and the

methods used to calculate storage resource/capacity were examined in this study. However, no new storage coefficients were developed for these systems because of the site-specific nature of the formation fluids and the production history of depleted hydrocarbon reservoirs as well as the fact that material balance equations will generally result in more accurate estimates of storage resource/capacity. DSFs occur over large regions of every continent and are often less well characterized than depleted hydrocarbon reservoirs. However, because of their large volume and wide distribution, DSFs have the greatest potential storage resource/capacity, and most of the efforts of this report went into the refinement of storage coefficients for these formations.

A clear and applicable resource/capacity classification system with consistent terms and definitions will be of great benefit for the advancement of CCS, particularly with respect to refining storage resource/capacity estimates. Previous classification systems developed for hydrocarbon and mining resources and commodities have limited applicability to CCS because their intent is to classify material removed from the ground as opposed to CO_2 storage within the material beneath the surface. Another issue to address is the notion of "undiscovered" resources, which does not really apply to saline formations since, for the most part, their location is known, however poorly they may be characterized. To address this, a classification system is proposed that combines concepts heralded by the CSLF technoeconomic resource pyramid (1) as well as the industry standard Petroleum Resource Management System (2). Also included are definitions from the DOE Carbon Sequestration Atlas of the United States and Canada (3), and concepts and definitions proposed by CO_2CRC in the report prepared for IEAGHG entitled "Aquifer Storage" (4). In addition, terminology was developed regarding the "area of assessment"—previously a combination of geological and geographical jurisdictions, which made comparison between assessment terms difficult. The geological/physical and geographical/political terminology concepts were split, and terms were developed for both hierarchies.

Through the examination of the published methods used to estimate storage resource/capacity in DSFs, a critical difference in storage resource/capacity results from the behavior of boundary conditions and whether the dominant process is the result of mobilization (as seen within open boundaries) or compression (as seen within closed boundaries). These two mechanisms represent two end points, as both processes will be present in a given storage scenario; however, the boundaries of the formation will cause one process to dominate over the other. Calculation of storage coefficients for both processes are described and addressed. Deterministic examination of the interplay of the two processes has not been developed, however. In the case of compression, efficiency is limited by an increase of pressure and the resulting compression of fluids and particles as well as the dilation of pore spaces. In the case of mobilization, the storage process involves the movement of natural formation fluids away from the injection site. Because of the relatively straightforward nature of the compressibility, closed-system method, the focus of this report has been on developing effective storage coefficients for open systems using both the DOE and CSLF methods.

Since previous work by CSLF has demonstrated that the DOE and CSLF methods for calculating CO_2 storage in open saline formations are nearly equivalent (5), the two methods were related to each other through a series of factors and equations so that storage estimates made with one system can be easily compared to the other. In the end, if the assumptions are made in a similar

manner, the resulting effective storage coefficients and estimates of effective storage resource made with one method can be easily related to the other through the following relationship:

$$E_E = C_C * (1 - S_{wirr})$$

Where E_E is the DOE effective storage coefficient, C_C is the CSLF effective storage coefficient, and S_{wirr} is the irreducible water saturation in the presence of CO_2 under reservoir conditions. Then when the storage coefficients are applied to their respective methodologies, the resulting effective storage resource calculated with each method will be equal:

$$V_{CO_2,CSLF_E} = V_{CO_2,DOE_E}$$

Where $V_{CO_2,CSLF_E}$ is the effective volume of CO_2 that can be stored under reservoir conditions as calculated using the CSLF methodology, and V_{CO_2,DOE_E} is the effective volume of CO_2 that can be stored under reservoir conditions as calculated using the DOE methodology. With this relationship in mind, a methodology was developed to determine the range of values for the effective storage coefficients at the site-specific and formation scales. This work was completed through a two-part effort, by first developing homogeneous models to test the relative strength of single variables on the effective storage coefficients and then by developing a series of heterogeneous models to develop a range for the effective storage coefficients for different lithologies, depositional environments, and structures. Ideally, the models would have been populated with properties from real-world CO_2 storage projects; however, since there are only a few large-scale CO_2 storage projects currently under way, a data set was developed based on hydrocarbon reservoirs. Considering that hydrocarbon reservoirs may reasonably be considered to be subsets of larger saline formations, the applicability of these hydrocarbon reservoir properties is appropriate. The data set, referred to as the Average Global Database (AGD), contains fluid and geologic properties from over 20,000 hydrocarbon reservoirs representing a wide variety of reservoir types from all over the world.

The strength and effect of five parameters—structure, relative permeability and irreducible water saturation, depth and temperature, vertical-to-horizontal permeability anisotropy, and injection rate/fluid velocity—were tested using homogeneous models, built based on the average properties from the AGD, to examine the effect of each parameter on storage efficiency and the resulting storage coefficients. In general, tightly closed structures, increased depth and lower temperatures, low ratios of vertical to horizontal permeability, and high injection rates/fluid velocity all increased the storage efficiency and the value of the storage coefficient. The effects of relative permeability and irreducible water saturation were much more subtle, with no large difference in the value of the storage coefficients with the relative permeability curves and irreducible water saturation values that were tested.

Values for the effective storage coefficients were developed for application to DSFs at the site-specific level using 195 different heterogeneous models based on the properties in the AGD for three different lithologies, ten depositional environments, and five structural settings. The resulting values for E_E and $C_C * (1 - S_{wirr})$ for the site-specific scenarios ranged from about 4% to about 17% with a 80% confidence interval, depending on the lithology, depositional environment, and structure. In each case, the structure played the largest role, with several of the

dome structures having an effective storage coefficient greater than 25%. The values developed for the site-specific level were extrapolated out to the formation scale for the three different lithologies, and values were determined for both the E_E and $C_C * (1 - S_{wirr})$ at the P10, P50, and P90 probability levels.

The values for storage coefficients and methodology developed over the course of this work can be applied at scales from the site-specific to the formation-level for both the DOE and CSLF open-system methodologies, and a technique is also presented which can be applied to closed systems. When performing an evaluation to determine the effective storage resource, there are two important issues that must be addressed: 1) the scale of assessment and 2) whether the majority of the storage comes from mechanisms associated with closed- or open-formation boundaries. If the evaluation is to be performed on an entire basin, then the effective storage resource should be calculated for each saline formation that has properties that make it amenable to CO_2 storage when the appropriate assessment methodology is applied. The resulting values should be added together to develop an effective storage resource for the entire basin.

Similarly, an assessment made over geographical/political areas should be estimated by evaluating the storage formations or portions of the storage formations separately, then adding the resulting effective storage resource estimates together to come up with the effective storage resource for the entire country, region, or state/province. This must be done since, in many cases, there are multiple stacked DSFs, each with its own unique properties, which could be used individually to effectively store CO_2 on a geologic time scale. Storage coefficients and resulting storage resource/capacity estimates calculated by any of the methods presented in this summary may be used to compare assessment areas in order to identify areas that may be suitable for further, more detailed studies. Storage coefficients calculated using any of the methods presented are not a replacement for the site-specific work required before the commencement of a large-scale storage project but are appropriate for first-order evaluations of the effective storage resource.

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Subtask 2.9 – Flame Characterization During Oxygen-Fired Combustion

Program Area:	CRD
Period of Performance:	7/1/09–9/30/10
Funding:	DOE: $60,000; Nonfederal: NA; Total: $60,000
EERC Subtask Manager:	Kirk Williams
DOE Technical Monitor:	Norman Popkie
Nonfederal Partners:	NA
Final Report:	Williams, K.D.; Gunderson, J.R. *Subtask 2.9 – Flame Characterization During Oxygen-Fired Combustion*; Final Report (June 29, 2009 – Sept 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-09-08; Energy & Environmental Research Center: Grand Forks, ND, Sept 2010.

In Subtask 2.9, thermal imaging methods were investigated to analyze flame and radiation characteristics and monitor NO_x and CO emissions formed during oxygen-fired combustion to determine the effects of controlling flue gas recycle rate (CO_2) and O_2 concentration on relative temperature, radiation, composition, and shape of oxy-fuel flames. Conventional air-fired flame parameters were evaluated and compared to the oxygen-fired flame parameters during oxygen-fired test runs as part of the first phase of the Partnership for CO_2 Capture (Subtask 2.5).

Three coals were selected for flame characterization: an Antelope PRB subbituminous coal, a Central Appalachian bituminous coal, and a North Dakota lignite from the Falkirk Mine. The flame characterization of these coals was to establish a broad cross section of the basic properties for comparison to the oxygen-fired testing. Representative coal samples were taken during each test as the coal fed from the hopper into the combustor. Proximate, ultimate, and heating value analyses were performed on the coal samples for each combustion test period. For each coal, a typical test consisted of a baseline air-fired test period followed by an oxygen-fired test. During all test periods, flue gas concentrations were recorded using in-line gas analyzers. In addition, heat capacity data were recorded using two heat flux probes located through the combustor wall. At the end of a test period, fly ash samples were removed from the ESP catch hopper, analyzed, and compared.

Thermal radiation is the predominant mode of heat transfer in the radiant zone of high-temperature, large-scale, particle-laden combustion systems such as pulverized coal-fired boiler furnaces. The medium in a pulverized coal-fired furnace is a mixture of gaseous products and suspended solid particles consisting of pulverized coal, char, fly ash, and soot. To collect the flame images in the combustor used for characterization, a real-time midband 3.5- to 5-µm infrared camera with a 3.9-µm flame bypass filter from FLIR Systems, Inc., was used. All of the thermal images were viewed through a 2- or 4-in. single-crystal sapphire viewport. Corrections for external optics energy transmission, temperature, humidity, and background radiation are accounted for during postprocessing.

Flame stability and flame shape observations between the normal air-fired and oxygen-fired test periods indicate the oxygen-fire conditions may tend to delay the combustion process by reducing the flame propagation velocity as a result of the increased heat capacity of CO_2, moisture, and ash in the recycled flue gas. For the purposes of this project, assessment of flame stability (which is a function of swirl) air flows (primary and secondary), fuel rank (volatility), and particle size, typically originates at the burner quarl. Thus the burner zone was the primary focus of the flame stability investigations. The delayed combustion can be substantiated by the thermal images showing a shorter, wider flame at the burner quarl, which is supported by the apparent cooler burner zone temperatures (from the thermal images) relative to the upper flame zones and the higher average heat flux temperatures at the upper probe location. However, the overall flame shape was difficult to accurately determine specifically in the upper zones because of limitations in what was imaged with the thermal camera. Thus the interpretations of the flame shape are limited to the burner quarl and the zone above the quarl.

Comparing flame shape in the thermal images between the two combustion modes indicates a more pronounced inner burner zone with more conical shape. The oxygen-fired combustion flame is a taller, more noticeable inner combustion zone that displays a lower observed temperature profile compared to the shorter, more compact flame displayed by the air-fired combustion condition. Flame propagation is different as the taller flame tends to move the combustion reaction further up into the upper combustor. Although the observed flame temperature does not appear to be significantly affected by the shape, the heat flux data suggest the greatest reaction zone may be occurring closer to the upper heat flux probe.

Apparent flame temperatures, as imaged by the camera, were limited primarily to an area around the burner-quarl zone. The actual flame temperatures are a function of location within the combustor and the specific flame emissivity in that combustion zone. Actual flame temperatures must be determined by a combination of calculations to account for changes in flue gas composition, emissivity, and suspended particulates. Because of similar firing conditions, the furnace exit gas temperature, as recorded by thermocouples in the flue gas stream at the upper portion of the combustor, does not give a clear indication of overall flame temperature differences between the two modes of combustion.

Heat flux data were collected during normal air-fired combustion and oxygen-fired test periods. Initial results indicate that heat flux in the lower combustion zone stays the same or decreases very slightly during oxygen-firing, while heat flux in the upper combustion zone is variable and appears to be based on fuel rank and flame shape. Although the heat flux of the lower probes appears to decrease under oxygen-fired combustion, based on the data collected, the heat flux of the upper probes is uncertain. However, the overall results do indicate that oxygen-fired combustion could have an effect on heat capacity, which could impact heat transfer on superheater surfaces in commercial boilers.

During oxygen fired combustion, the stack NO_x emissions were reduced by up to 80% as compared to normal air-fired combustion with the same fuel. Results also indicate as the burner swirl number increases (from 2.5 to 3.5), NO_x emissions at both the stack and the furnace exit increase on a ppm and lb/MMBtu basis. When overfire air (OFA) is introduced during oxygen-fired combustion, the NO_x emissions remain relatively similar on a lb/MMBtu basis. Overall, small

changes in OFA flow rates and in oxygen flow distribution, such as decreasing primary oxygen flow, appear to have little effect on NO_x emissions as recorded at the stack.

Fly ash was collected from the ash hopper of the ESP for both oxygen-fired and air-fired test periods. This ash was analyzed using x-ray fluorescence to determine the effects of oxygen-fired combustion on ash composition, specifically in the generation of carbonates in the fly ash as a result of the high CO_2 concentrations (85%–90%) of the flue gas. Based on the analytical results, no carbonates were formed in the ash, and the results from a comparison between the oxygen-fired test periods to air-fired test periods indicate no major differences were observed and generally conclude that oxygen-fired combustion may not have much of an effect on ESP ash composition.

Subtask 2.10 – Capitalizing on CO_2 Storage in Lignite Coal: Biological In Situ Methane Production

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $80,000; Nonfederal: NA; Total: $80,000
EERC Subtask Manager:	Darren Schmidt
DOE Technical Monitor:	Andrea McNemar
Nonfederal Partners:	NA
Final Report:	Schmidt, D.D. *Subtask 2.10 – Capitalizing on CO_2 Storage in Lignite Coal: Biological In Situ Methane Production*; Final Report (July 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-18; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

Subtask 2.10 was undertaken to investigate microbially enhanced CBM production from a CO_2 sequestration pilot test conducted in a lignite coal reservoir in North Dakota. The effort focused on potential revenue-generating strategies for coal-based carbon storage projects. The objective was to identify economically viable sources of "hydrogen-containing fluids" that can be pumped into a storage reservoir to provide a microbial substrate for methane production.

Subtask 2.10 supported previous efforts under Subtask 1.4. Previous work indicated the presence of methanogenic bacteria in coal and some potential for methane production; however, the methane production is limited to the conversion of substrates, including acetate, formate, methanol, and H_2/CO_2. The substrates can be created from carbon-reducing bacteria that break down coal. Samples previously analyzed failed to identify carbon-reducing bacteria. Therefore, this project was targeted at identifying economically viable sources of hydrogen that can be injected with CO_2, which can allow methanogenic bacteria to produce gas from an in situ bioreactor. The premise was to determine the proper approach to enhance methane production, engineer a feasible approach for injection/production, and analyze the economics.

Coal seams are a potential target for the geologic sequestration of CO_2. The injection of CO_2 into coal has the potential to produce methane normally referred to as ECBM. The mechanisms of

ECBM include the injection of gases (CO_2/N_2) into a coal reservoir, adsorption of the injected gas onto the coal, desorption of methane, and production of gas through a well to the surface. Further enhanced methane production may be possible by means of microbial activity in the coal reservoir. Microbially enhanced CBM has the potential to increase domestic sources of natural gas and is the frontier technology in CBM.

With the objective of identifying economically viable sources of hydrogen-containing fluids that can be pumped into a storage reservoir to provide a microbial substrate for methane production, fluids were identified within the Williston Basin, representing industrial wastewater, municipal wastewater, agricultural processing (ethanol and sugar), and animal manure (swine). These fluids were screened in the laboratory for methane generation potential. The results from the screening tests appear to indicate that animal manure and municipal wastewaters are good candidates for microbial methane production. The estimated total for animal manure in the state of North Dakota at the time of this study was 1.6 million tons/year, whereas municipal sludge was estimated at 26,000 tons/year. In either case, aggregated collection would be required and would present challenges. Although the screening experiment did not favor the sugar-processing wastewater, the calculated values from the analytical work show high volumetric methane generation potential. The benefits of sugar-processing wastewater are the proximity (Sydney, Montana), single source (1 million tons/year), and benign nature of the water chemistry (sucrose). The poor performance for the sugar plant wastewater was most likely because of low pH, and this was most likely because of the presence of volatile fatty acids at inhibitory concentrations. Future work could benefit from considering analysis of higher-strength agricultural processing waters.

Subtask 2.11 – CO_2 Capture with Aqueous Froth

Program Area:	CRD
Period of Performance:	6/1/10–5/31/11
Funding:	DOE: $60,000; Nonfederal: NA; Total: $60,000
EERC Subtask Manager:	Edwin Olson
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Olson, E.S. *Subtask 2.11 – CO_2 Capture with Aqueous Froth;* Final Report (June 1, 2010 – May 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-05-06; Energy & Environmental Research Center: Grand Forks, ND, Aug 2011.

The objective of Subtask 2.11 was to develop a novel system for the capture of CO_2 from a low-SO_2 gas stream such as a postcombustion flue gas or fuel gas stream. The Peletex aqueous froth CO_2 ($AFCO_2$) scrubber captures gaseous CO_2 from postcombustion flue gas with high efficiency, owing to rapid mass transfer at the bubble interface, and sequesters the captured CO_2 by direct mineral carbonation in one unit operation. The $AFCO_2$ is efficient, but it could be operated at lower cost with an alternative scrubbing reagent comprising magnesium hydroxide. Rates of CO_2 capture in the froth scrubber were evaluated in this project using a magnesium oxide reagent for the capture operation.

Several schemes for CO_2 capture are possible. One is to recycle the precipitated magnesium carbonate, which requires dewatering and heating to 375°–400°C to regenerate magnesium oxide. Alternatively, precipitated magnesium carbonate is dewatered and, depending on the morphology and composition, either landfilled or used for producing high-strength concrete, insulation, or other products. Although $MgCO_3$ requires heating to 375°–400°C for decarboxylation and regeneration of MgO, it is less endothermic (118 kJ/mol) than $CaCO_3$ decomposition (178 kJ/mol). A third option is to recycle the soluble magnesium bicarbonate product by mild heating of the aqueous solution to liberate CO_2 and form insoluble magnesium carbonate, which is recycled. These options were evaluated in the project.

The key to economic success is a low-cost process for preparing the magnesium oxide used as the basic reagent slurry in the froth capture device. In this project, a proprietary method for extraction of magnesium from ultramafic rocks was tested to provide the low-cost MgO. This differs from earlier approaches where stronger and more corrosive acids were used in the extraction and expensive bases were added in some cases to neutralize the magnesium salt.

Magnesium oxide was obtained in reasonable yield by extraction from serpentine and olivine dunite with sulfurous acid, followed by calcining. More severe conditions gave iron-contaminated product. This extraction used an inexpensive and less corrosive acid reagent and did not require any neutralization step. This route represents a substantial improvement over prior methods for preparing an effective reagent slurry for the capture process and should lead to a lower-cost process.

The magnesium oxide extracted from serpentine was effective in capturing CO_2 in the Peletex froth absorber. The serpentine-derived MgO and recycled MgO were at least as effective as commercial MgO. Low capture rates were achieved at ambient temperature but improved significantly at 37°C.

The slurry (floc) of hydrated magnesium carbonates resulting from the capture was difficult to settle. However, a major finding of this investigation was the discovery that the settling was improved by adding calcium oxide or, to a lesser degree, by adding a humate agglomerator. The CaO addition thus allows the clear aqueous phase to be easily decanted, and the dewatering step occurs much more easily.

Mixtures of hydrated magnesium carbonates were formed in the CO_2 capture with the Mg reagent. No oolitic forms were found. There is little reason to expect the solid products will be useful for concrete products, although other cementing products could be prepared. Only a small amount of dolomite formed from the carbonation of the mixture of MgO and CaO. Most of the magnesium carbonates and calcium carbonates are separate phases.

Regeneration of the magnesium oxide from the magnesium carbonate hydrates was effected at 400°C. This is less than half of the regeneration temperature of $CaCO_3$ (which requires greater than 800°C temperatures for regeneration). Unfortunately, it still represents a parasitic load that cannot be met with waste steam.

A portion of the products (15%) occur as soluble magnesium bicarbonate. The bicarbonate solution was converted to hydrated magnesium carbonates at low temperature (80°C). Since this operation results in the evolution of CO_2, a cycle based on magnesium carbonate capture of CO_2 to form the bicarbonate and low-temperature regeneration of carbonate with low-pressure utility steam is feasible; however, since only small amounts of magnesium bicarbonate are soluble, this process would require heating a large amount of the solution.

This preparation of magnesium sulfite from olivine or serpentine can be used effectively as the magnesium source for other processes such as the magnesium-enhanced lime capture of SO_2, but only CO_2 capture was investigated in this subtask.

Subtask 2.12 – CO_2 Reduction by TiO_2

Program Area:	CRD
Period of Performance:	7/1/10–12/31/11
Funding:	DOE: $100,000; Nonfederal: NA; Total: $100,000
EERC Subtask Manager:	Melanie Jensen
DOE Technical Monitor:	Arthur Baldwin
Nonfederal Partners:	NA
Final Report:	Jensen, M.D.; Cowan, R.M. *Subtask 2.12 – CO_2 Reduction by TiO_2*; Final Report (July 1, 2010 – Dec 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-12-11; Energy & Environmental Research Center: Grand Forks, ND, Dec 2011.

With the increased demand for carbon capture and conversion technologies, Subtask 2.12 was underetaken to prove that CO_2 could be reduced to a hydrocarbon (i.e., CH_4) in the presence of water vapor and TiO_2 photocatalyst and to generate data that could support the scale-up feasibility of the technology. Activities to meet these goals included the design and assembly of a laboratory-scale test system, the performance of experiments aimed at verifying the concept and evaluating the impacts of various factors on the production of CH_4, and a cursory determination of the extent to which the TiO_2 is deactivated and can be regenerated.

Work by other researchers indicated that CH_4 yields from a closed, gas-filled system would be very small. It was postulated that more CH_4 could be produced in a fluidized-bed system. A laboratory-scale fluidized-bed system was designed, fabricated, and shaken down. It was found that the TiO_2 is too friable to withstand fluidization, breaking up into fine dust that plugged exhaust ports, limited ultraviolet (UV) penetration, and was carried out of the reactor with the CO_2 stream. In addition, the CO_2–water vapor flow rate required for fluidization was sufficiently high that it diluted any CH_4 that was produced to below detection limits.

Because of the difficulty encountered with the variations in flow-through designs that were tested while trying to address various operational issues, it was determined that a simple closed-vessel design should be considered, and a test system was fabricated. The experiments were performed according to a full factorial matrix. Four variables were thought to affect the production

of CH_4: light wavelength available to the reactants (i.e., the transmissivity of the reaction vessel material), light spectrum available (i.e., use of light sources having different spectral emission patterns), temperature (which affects the amount of water present at the interface between the TiO_2 photocatalyst and the CO_2), and reaction time. Experiments at center point conditions were also included to provide estimates of the precision and a measure of the curvature of the results. The center point results also provided a means for detecting any deactivation of the TiO_2 photocatalyst with time.

Three reaction vessel types were evaluated, each of which allowed transmittance of light over a different range of wavelengths. The glass types included premium synthetic fused quartz, economy fused quartz, and soda–lime–silica glass (regular glass). Bulbs that simulated natural sunlight with a full spectrum in the visible range, black lights that produced light in a very narrow spectrum centered at 366 nm, and the combination of simulated sunlight and black light were tested. Testing was performed at three different temperatures to see if the amount of water in the vapor phase would impact the CH_4 production. Finally, three reaction times were evaluated: 24, 36, and 48 hr.

The results of the experiments were statistically analyzed, but the statistical package could not produce a mathematical equation showing that any of the variables affected the production of CH_4. All of the variables were examined, and the light sources seemed to be the only variable that could be problematic. Using a light intensity meter, it was found that the sunlight-simulating bulbs were much less intense than the black lights over the expected range of activity. This phenomenon explained why the statistical package could not produce a mathematical model from the data. A new matrix was developed that used only black lights with the light intensity varied by distance of the reactors from the light source.

The data from the second matrix were analyzed using the regression analysis package included in Microsoft Excel 2007. The equation (model) that best predicted the CH_4 concentration is:

$$CH_4 \text{ Concentration} = 0.008698921 + (0.004933113 \times [(\text{Time} - 36)/12]) + (0.000998347 \times [(\text{UV-400})/100]) + (0.005308891 \times [(\text{UV-400})/100]^2)$$

The model indicates that the production of CH_4 is affected by the length of reaction time and the UV intensity. The temperature (i.e., how much water is present in the vapor phase) and the reactor material did not significantly impact CH_4 production for the closed reactor system. When plotted over the UV intensity and reaction time ranges that were evaluated, the model indicates that the CH_4 concentration could be expected to reach a maximum of about 0.02 mol% at the highest UV intensity (500 $\mu W/cm^2$) and the longest reaction time (48 hr). It is possible that more CH_4 could be produced at higher intensities for longer times, but the increased yield would probably not be large, even for tests of a reasonable length.

Photocatalyst deactivation was evaluated empirically by observing changes in CH_4 production with time. The TiO_2 was used for 492 hr with no noticeable degradation in CH_4 production. A test employing TiO_2 that had been used for 192 hr resulted in virtually the same amount of CH_4 as produced by previously unused TiO_2.

This study found that it is possible to produce measureable amounts of CH_4 by reacting CO_2 with water vapor in the presence of TiO_2 photocatalyst and UV light. The TiO_2 photocatalyst does not seem to deactivate during use exceeding 490 hr. However, the CH_4 formation rate in a closed system is very small. Although it is possible that CH_4 formation rate might be higher in a fluidized-bed system than a closed system, the TiO_2 photocatalyst is very friable and would be reduced to powder very quickly in a fluidized bed. Fines would entrain in the gas flow and be quickly lost from the reactor. In addition, it is possible that a dusty environment could limit the UV light penetration, minimizing the CO_2-to-CH_4 reaction near the walls of the reactor farthest from the light source.

The approach studied in this work does not appear to offer a commercially viable means of producing CH_4.

Subtask 2.13 – Evaluation of Novel Technologies for CO_2 Capture

Program Areas:	SNESS and CC
Period of Performance:	10/1/10–2/28/13
Funding:	DOE: $1,671,972; Nonfederal: $713,871; Total: $2,385,843
EERC Subtask Manager:	Brandon Pavlish
DOE Technical Monitor:	Vito Cedro
Nonfederal Partners:	Alberta Innovates – Energy and Environment Solutions, CO_2 Capture Project Consortium (BP, Chevron, Eni, BR Petrobas, Shell, and Suncor), NDIC, Neumann Systems Group (NSG), NPPD, and University of Wyoming
Final Report:	Pavlish, B.M.; Kay, J.P.; Fiala, N.J.; Stanislowski, J.J. *Subtask 2.13 – Evaluation of Novel Technologies for CO_2 Capture*; Final Report (June 15, 2010 – Feb 28, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-02-06; Energy & Environmental Research Center: Grand Forks, ND, Feb 2013.

Subtask 2.13 comprised an evaluation of the NSG NeuStream™-C system, an advanced gas contactor, which has the potential to significantly reduce the cost of postcombustion solvent-based CO_2 capture. The system, which consists of a three-stage absorber and four-stage stripper, was designed and built by NSG and installed at the EERC's CTF. The system uses a proprietary contacting system that has been shown to reduce costs at the bench-scale level.

The objectives of this project were to:

- Design and fabricate the pilot-scale NeuStream-C system.
- Perform system design verification.
- Integrate and install the NeuStream-C system on the EERC CTF.

- Perform shakedown and initial verification testing.

- Perform system baseline testing.

- Define and design system modifications for optimization based on baseline testing.

- Perform system optimization testing including testing of multiple solvents from other technology suppliers.

- Evaluate and compare baseline testing results to the current results of the EERC's conventional solvent system.

- Perform an economic analysis of the system at different points in the optimization to determine feasibility.

- Perform a sensitivity analysis to include the parameters of importance when considering scale-up.

The system was designed, fabricated, and verified by NSG during the spring and summer of 2011. Integration and installation of the system at the EERC occurred at the beginning of September 2011, and shakedown testing commenced at the beginning of October 2011.

Shakedown testing was conducted for 9 days and was successful in that operational problems were identified and resolved for future testing. Testing was performed at the EERC using the pilot-scale NeuStream-C system on a 100–260-scfm stream of coal-derived flue gas. The baseline solvent used for this project was 30 wt% MEA with water.

System calibration and baseline testing were conducted from November 7 to 10, 2011. During this phase of testing, the CO_2 capture rate varied from 30% to 50% depending on conditions. Several modifications were made to the NSG stripper after this run to improve performance, including the addition of extensions to the stripping sections.

Optimization testing began with a test run on December 19–20, 2011. On the first day of testing, the NSG absorber was paired with the EERC's conventional stripper, and on the second day, the NSG absorber was used with the NSG stripper. At a 190-scfm flue gas flow rate, both systems achieved CO_2 capture rates in the 40% to 50% range, and the working capacity of the solvent was 0.07, indicating that further improvements needed to be made to the stripper. A model of the NSG system was created that confirmed this hypothesis.

During the next optimization run, from January 9–11, 2012, both the solvent flow rate and the flue gas flow rate were varied to determine the performance of the NSG system at different conditions. A solution of 30 wt% MEA with water was used as the solvent. The best CO_2 capture numbers were achieved for high solvent flow rates and lower flue gas flow rates, with a maximum capture rate of 80% at 90 scfm and 15 gpm. However, the working capacity remained flat as process conditions changed, indicating that further changes needed to be made to the stripper.

Before the next optimization run, an additional heat exchanger was added between the absorber and the first stripper section to increase the amount of heat in that area of the stripper and improve performance.

Two solvents, 30 wt% MEA with water and 8 M piperazine, were used for the next optimization run, which was conducted from February 27 to March 2, 2012. Maximum CO_2 capture rates obtained during this run were approximately 75% for MEA and 90% plus for 8 M PZ. During this run, an absorber modification was also tested to see if higher flue gas velocities would affect efficiency. The absorber modification did not have any apparent effects, either positive or negative, on system performance.

Two final weeks of testing in mid- to late 2012 looked into two final changes to the stripper operation: giving independent heat to each stripper vessel and allowing independent control of each vessel, essentially allowing it to be operated in a two-stage flash configuration. These changes improved the lean loading of the solvents, reducing the loading to levels expected during typical operation. This resulted in improved performance of MEA, raising the capture rate to over 85%. Performance of 8 M PZ was limited because of difficulties maintaining steady state during limited testing.

Performance of the system is an improvement over traditional systems in that the specific surface area has been increased from 100 to 200 to almost 300 m^2/m^3. Additionally, the gas flow through the system can be increased with no significant pressure penalty.

Subtask 2.14 – Beneficial Use of CO_2 for North Dakota Lignite-Fired Plants

Program Area:	CRDP
Period of Performance:	2/1/11–1/31/12
Funding:	DOE: $134,040; Nonfederal: $254,345; Total: $388,385
EERC Subtask Manager:	Jason Laumb
DOE Technical Monitor:	Darin Damiani
Nonfederal Partner:	NDIC
Final Report:	Laumb, J.D.; Cowan, R.M.; Azenkeng, A.; Hanson, S.K.; Heebink, L.V.; Letvin, P.A.; Jensen, M.D.; Raymond, L.J. *Subtask 2.14 – Beneficial Use of CO_2 for North Dakota Lignite-Fired Plants*; Final Report (Oct 1, 2011 – Jan 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-01-27; Energy & Environmental Research Center: Grand Forks, ND, Jan 2012.

In Subtask 2.14, a study was undertaken to identify the most promising technologies for the use of CO_2 produced by North Dakota's lignite-fired utilities. Several activities were performed, including summarizing current CCS technologies, conducting a survey of current CO_2 use technologies, determining how applicable the technologies would be to North Dakota lignite, identifying the likely best technology options for North Dakota lignite, performing preliminary market assessments for potential products, and providing an indication of the economic benefit of

the best technology options for North Dakota lignite users. The information collected and documented in this report was designed to answer the questions, What CO_2 use technologies exist or are under development? How much of the CO_2 from coal-fired power plants can they use? and Do any of them have the potential to make money or at least help offset some of the costs of CO_2 capture?

There are three CO_2 capture technology platforms: precombustion capture, capture during combustion, and postcombustion capture. Capture during combustion is often referred to as oxyfiring or oxycombustion because one of its approaches involves the use of pure oxygen rather than air as the source of molecular oxygen that is fed to the boiler. In general, precombustion capture yields high-purity, high-pressure CO_2; combustion capture yields purified low-pressure CO_2; and postcombustion capture yields high-purity, low-to-moderate pressure CO_2. Some beneficial-use technologies can be used to provide for postcombustion capture.

CO_2 use technologies can be divided into six broad categories:

- Direct use of CO_2
- Mineralization of CO_2
- As a feedstock in the manufacture of chemicals that require the reduction of the carbon to a less oxidized form
- As a feedstock in the manufacture of chemicals that do not require chemical reduction of the carbon
- Photosynthesis-based technologies
- Novel technologies

Direct-use technologies include use of CO_2 for EOR, ECBM production, and as a solvent, refrigerant, or in foods and beverages. These technologies are well known, have been extensively documented elsewhere, and the Lignite Energy Council (LEC) specifically excluded them from being considered as part of this project. However, it should be noted that the supply of CO_2 for EOR and ECBM projects could represent a good near-term opportunity for North Dakota lignite users.

Mineralization to form products from CO_2 is a relatively new concept. It is the formation of a carbonate or bicarbonate solid from CO_2; thus the CO_2 becomes a part of the solid product. CO_2 captured from any source can be used as a feedstock for mineralization reactions. The process also requires a source for the alkalinity required by the reaction; lignite fly ash could potentially provide this alkalinity. The most advanced of the mineralization technologies is still only at a pilot scale of development, and the products that will be generated by the various technologies, should they become commercial, are more likely to fill niche markets than be widely employed.

Nineteen mineralization technology developers were identified. Most of the companies working in the area of CO_2 mineralization have provided lists of potential products but have not provided a clear path to making and marketing those products. The market will dictate the type and quantity of products that are made. The entry-level product for most mineralization companies will likely be aggregate that can be used for roads and/or as a component of concrete. Although the concept shows promise, it does not appear to offer an economically viable opportunity for the lignite industry in the near term because 1) aggregate made from mineralization of CO_2 is estimated to cost roughly double the current rate for gravel aggregate because of the value of the materials required to supply the metal cations and alkalinity for the mineralization and 2) lignite fly ash is more valuable as a raw material used for solidification of waste pits in the western North Dakota oil fields than as a source of alkalinity for mineralization reactions.

CO_2 can be used in the production of chemicals and fuels. Many approaches are being developed to use CO_2 captured from various sources to produce useful fuels, chemical feedstocks, and in the direct conversion of CO_2 to chemical products such as polycarbonate plastics or urea. The potential for these technologies to use CO_2 from coal-fired power plants is limited because 1) substantial energy input is needed to convert the carbon in CO_2 from its fully oxidized state into a reduced state where it can serve as a fuel and 2) the industries using CO_2 as a feedstock in chemical production also perform upstream processes that produce CO_2 either directly (typically at high temperature and pressure) or when they consume fuel in order to provide energy for the overall process.

The status of CO_2 reduction to fuels is currently limited to research and development studies mostly in academic laboratories. When a fuel is made from CO_2, energy is used to reduce the carbon from a fully oxidized state to a more reduced state. The amount of energy required for this reduction process is greater than the amount of energy that can be obtained either from the process or from use of the newly produced fuel. A CO_2-to-fuel process only makes sense where the product formed is of very high value, the fuel is used as a storage product made from an intermittent energy supply source (e.g., wind, solar), and/or the fuel produced is useful in ways that the original source fuel was not (e.g., production of a transportation fuel from coal-derived CO_2).

When CO_2 is directly converted into chemicals, it is reacted with another feedstock that had to be produced in an upstream process. The quantity of CO_2 produced in this upstream process along with the CO_2 produced from energy generation associated with this upstream process will exceed the CO_2 demand of the step that uses CO_2. Therefore, most companies performing these processes will not use externally supplied CO_2. Additionally, most of the CO_2 use processes, or the upstream processes used to generate the reactive intermediates, require reaction conditions such as high pressure and/or high temperature, with fossil fuel combustion typically used to provide the heat and power necessary to meet these needs. In fact, more CO_2 is produced during polycarbonate plastic or urea production than is used to make the products. Some of the largest postcombustion CO_2 facilities operating in the world are located at urea plants where CO_2 is captured from natural gas combustion flue gas in order to supply some of the CO_2 used for converting ammonia to urea.

Photosynthesis-based processes using externally sourced CO_2 include algae production and greenhouse agriculture. In order for these technologies to provide a favorable CO_2 demand, the

energy input for CO_2 reduction to organic carbon needs to be primarily from sunlight rather than from electric lights unless the electricity is derived from a zero-carbon source (i.e., wind, solar, nuclear). Greenhouse agriculture and algae systems can use low-concentration CO_2 streams. In algae production, CO_2 must be supplied both as a source of carbon for growth of the algae and to control the pH of the growth media. In greenhouse agriculture, CO_2 serves as the carbon source for plant growth and can increase plant growth rates. CO_2 supply to greenhouses is particularly important in colder climates where increasing air exchange to supply CO_2 from the outside air would result in excessive heating costs.

The microalgae production industry is a small and well-developed industry that has a proven ability to make money. The industry purchases externally sourced CO_2, but the size of its markets is small relative to the amount of CO_2 that is potentially available from power plants. Less than 20,000 tons/yr (18,150 tonnes/yr) of algae is produced worldwide, primarily for use as nutritional supplements (1). There has been a recent explosion of algae start-up companies (some estimate more than 200 since 2005) that are trying to break into potential algae product markets that promise to be much larger than the nutritional supplement market but require much less expensive algae. These larger markets include the production of biofuels, animal feeds, and fish meal replacements. Since these products have a relatively low value, production costs must be substantially reduced from current commercial production costs. Production of these lower-value products cannot be performed in an economically viable manner even under the most favorable conditions.

Algae and microalgae technologies are not economically feasible for North Dakota. The successful algae-producing companies are located in environments that favor the manufacture of their products (i.e., moderate temperatures and sunlight are available without extra cost). Their high-value nutrient supplement products are dry, shelf-stable and, therefore, relatively inexpensive to transport, making them readily available to the local population even without local producers. Irrespective of location, algae and microalgae products that could use a substantial amount of CO_2 (e.g., fuels and feed) are currently more expensive to produce than their potential market value can fetch.

Greenhouse agriculture, or controlled-environment agriculture, involves growing plants in a greenhouse. High-technology greenhouses are supplied with CO_2, heat and humidity control, and supplemental light as required to ensure high productivity. The common products from this type of agriculture include flowers, specialty fruits, and vegetables. North Dakota power plants may potentially benefit from the development of greenhouse agriculture operations in the state. These facilities can use both CO_2 and low-grade heat from the power plants and will also be customers for electricity used in supplemental lighting. The total demand for CO_2 is unlikely to be high, but the market and economic indicators investigated appear to indicate that a profitable venture could be developed based on this CO_2 use technology.

Twelve novel CO_2 use technologies were evaluated. These are primarily conceptual and laboratory-scale proof-of-concept processes of the type being supported by DOE's ARPA-E (Advanced Research Projects Agency-Energy) Program. They include processes that involve the electrochemical conversion of CO_2 to fuels and/or other chemicals, bioelectrochemical systems such as reverse microbial fuel cells that combine microbial processes and electrochemistry to produce chemicals, the use of microorganisms that convert H_2 and CO_2 to desirable chemicals,

and other processes that use sunlight to power chemical synthesis reactions. All of the novel CO_2 use technologies are at a very early stage of development and are not close to moving out of the laboratory. In addition, these processes require the input of energy to convert CO_2 into a useful product. The hope is that some of these concepts will, at the very least, contribute to the development of useful technologies that can be commercially relevant sometime in the future, perhaps within the next 25 years. A great deal of work and the investment of substantial time and money will be required if that is to happen.

The amount of CO_2 produced by North Dakota lignite-fired power plants dwarfs the needs of any of the use technologies, even if they were to be performed on a very large scale. The technologies that can use flue gas concentrations of CO_2 as the source (assuming it has been cleaned of contaminants that might harm the process or product) include some mineralization technologies and photosynthesis technologies. Some of the novel technologies may also fall into this category, although their early stage of development makes this unclear at best. Most of the direct use (i.e., EOR and ECBM operations) and chemical synthesis technologies require high-purity, high-pressure CO_2.

Very few CO_2 use technologies appear to be viable possibilities for North Dakota lignite-fired power plant CO_2. The novel technologies are too early-stage, and the chemical technologies do not require externally sourced CO_2. Algae and microalgae technologies are not economically feasible in North Dakota. Mineralization technologies suffer from the lack of a well-defined product and the current economics that estimate that any products would be more expensive than those that are currently available. Greenhouse agriculture appears to be the only promising technology that is currently both technically and economically feasible in North Dakota.

Greenhouse agriculture is not expected to use more than a very small fraction of the CO_2 produced by North Dakota power plants, but it has potential because of the high market value of its products. Facilities would be required to offer supplemental heat and lighting for many months each year, but the productivity of such greenhouses is several times higher than traditional farming, so the extra cost could be recovered through the sale of the additional product. Transport of fresh produce to North Dakota and surrounding states and provinces from other locales is expensive, and the market study confirmed that consumers and food distributors preferred locally sourced, high-quality vegetables to the imports.

This study showed that there are three potential opportunities for use of CO_2 produced by the lignite-fired power plants in North Dakota: supply of captured, compressed, and purified CO_2 for use in EOR and/or ECBM operations; mineralization; and greenhouse agriculture.

Reference

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Subtask 2.15 – Extraction of Formation Water from CO_2 Storage

Program Area:	CRDP
Period of Performance:	5/1/11–6/30/12
Funding:	DOE: $35,000; Nonfederal: $60,937; Total: $95,937
EERC Subtask Manager:	Ryan Klapperich
DOE Technical Monitor:	Andrea McNemar
Nonfederal Partner:	IEAGHG
Final Report:	Klapperich, R.J., Cowan, R.M., Gorecki, C.D., Liu, G., Bremer, J.M., Holubnyak, Y.I., Kalenze, N.S., Botnen, L.S., Saini, D., LaBonte, J.L., Knudsen, D.J., Stepan, D.J., Steadman, E.N., and Harju, J.A., 2012, Extraction of formation water from CO_2 storage: Final report (May 15, 2011 – June 30, 2012) for IEA Greenhouse Gas R&D Programme and Subtask 2.15 of U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2012-EERC-06-06, Grand Forks, North Dakota, Energy & Environmental Research Center, June.

In Subtask 2.15, the use of extracted water on a commercial scale was evaluated using data from four existing and potential real-world storage projects. DSFs constitute the largest potential global resource for the geologic storage of CO_2. Their use is, in turn, crucial to the successful scale-up of storage from pilot and demonstration projects to commercial operations. Extraction of saline waters from CO_2 storage formations is a potential method to improve reservoir storage volume, manage CO_2 plume migration, reduce cap rock exposure to CO_2, manage storage reservoir pressure, and/or generate a new source of water for a variety of beneficial surface uses. Indirect benefits derived from the treatment and sale of the extracted water may also provide additional economic incentives or cost offsets for formation water extraction.

This project used hypothetical injection scenarios to demonstrate the impact of formation water extraction at realistic locations. The sites—the Teapot Dome Field in the United States, the Zama Field in Canada, the Gorgon site in Australia, and the Ketzin site in Germany—represent a range of geologic storage targets, reservoir water quality, injectivity, climates, populations, and water use opportunities. Geologic models were constructed on potential storage targets, encapsulating their geologic properties, structure, and heterogeneities based on published data. A variety of CO_2 injection and formation water extraction scenarios were simulated to understand the nature of water extraction and its effects on CO_2 storage and plume behavior, including its effect in a closed system (Zama Field). Estimated rates of water extraction were derived from these simulations for analyzing their potential use at both industrial and domestic surface facilities. In addition, simulations were developed to test the possibility of mixing CO_2 with extracted water at the surface prior to injection.

The simulation results showed that the CO_2 storage capacity increased with the formation water extraction for all test sites. The volumetric ratio of CO_2 injection/water extraction was about 1:1 for most of the cases with pure CO_2 injection. This resulted in increased storage capacity for all sites, ranging from a 4% increase at Gorgon (where reservoir capacity vastly exceeded

injection/extraction capability) to 1300% at Zama (a closed system restricted by pressure limitations of the cap rock). Water extraction approximately doubled storage capacity at both Ketzin and Teapot Dome, 197% and 204%, respectively, where reservoir conditions limited injection rates. At Ketzin, it was found that a larger quantity of CO_2 could be injected (a 250% capacity increase) if the injector and extractor were used as injection wells. Additional simulations with up to 12 injectors and 13 extractors revealed that, with a larger quantity of wells, water extraction could have a greater impact on potential storage than injecting through all wells. However, in the Teapot Dome site, the use of an injection–extraction pair was found to produce a larger storage capacity than two injectors. Because of the presence of a relatively thin injection zone, the simulations were repeated with horizontal wells, but the injection–extraction pair outperformed the two injection wells. Storage capacity was increased by 367% with the horizontal pair over the base case injection. As a result, it can be said that water extraction can significantly increase the available capacity of a reservoir, but because of the wide variety of geologic and engineering variables involved in large-scale CO_2 storage, it may not be the most efficient use of resources in all cases.

Simulations were developed for two of the case study sites to investigate and compare the utility of injection of CO_2-saturated water, and it was found to require much greater volumes of extracted water while only storing a small fraction of the CO_2 that could be injected as supercritical CO_2. It may be possible to use this approach for storage in more shallow saline formations where the pressure is subcritical for CO_2; however, with decreasing pressure comes decreasing solubility of CO_2, reducing the quantity of CO_2 that can be dissolved in the shallower saline formations. The associated technical challenges with maintaining CO_2 in solution through the changing pressure–temperature conditions from surface facilities to injection point and managing the potential scaling and corrosion possibilities further limit the economic utility of this practice.

The quality of extracted waters from the case study sites, and indeed all potential storage formations, varies greatly from low-salinity waters (<10,000 ppm total dissolved solids [TDS]) to very high salinity waters (>200,000 ppm TDS). The possibility of treatment for beneficial use is economically restricted to the lowest salinity waters because of the cost of desalinization. Economically viable waters were identified at Gorgon (10,000–20,000 ppm TDS) and Teapot Dome (10,000 ppm TDS), where treatment costs were estimated to range from US\$0.76/m^3 to US\$0.88/m^3 and US\$0.73/m^3 to US\$1.06/m^3, respectively. Input flow rates of extracted water are the greatest influence on these prices because of economies of scale. These figures are regionally competitive but do not include the cost of transportation which, in the Gorgon site, more than doubles the cost of the water. Treatment for beneficial use of water is unlikely at Ketzin and Zama because of high salinities. The relatively high quality of water from the Gorgon site makes ocean disposal an option as well, in accordance with local regulations.

Formation water extraction from CO_2 storage reservoirs is applicable for increasing storage capacity, managing reservoir pressure, and controlling plume movement. Analysis of the resulting water quality and quantity, available treatment technologies, and potential transportation costs reveals there is likely to be limited potential for the beneficial use of extracted water from CCS facilities. Although variable by location, the difference between the highest quality of water appropriate for CO_2 storage and the lowest quality of water economically viable for treatment and beneficial use is relatively small, ruling out a large majority of potential storage targets whose

water quality exceeds those treatment limits. Ideal circumstances of relatively high quality reservoir water and highly stressed or limited regional water resources will need to coexist before beneficial use of extracted water should be considered. Additional work classifying the water quality of potential DSF storage targets is necessary before these conclusions can be revisited.

Subtask 2.16 – Cancelled

Subtask 2.17 – CO_2 Storage Efficiency in Deep Saline Formations

Program Area:	CS
Period of Performance:	5/1/13–4/30/14
Funding:	DOE: $35,000; Nonfederal: $60,937; Total: $95,937
EERC Subtask Manager:	Charles Gorecki
DOE Technical Monitor:	Andrea McNemar
Nonfederal Partner:	IEAGHG
Final Report:	Gorecki, C.D., Liu, G., Braunberger, J.R., Klenner, R.C.L., Ayash, S.C., Dotzenrod, N.W., Steadman, E.N., and Harju, J.A., 2014, Subtask 2.17 – CO_2 storage efficiency in deep saline formations: Final report (May 1, 2013 – April 30, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2014-EERC-08-12, Grand Forks, North Dakota, Energy & Environmental Research Center, August.

In Subtask 2.17, volumetric and dynamic CO_2 storage resource-estimating methods used to evaluate the storage potential of DSFs were compared to investigate the applicability of using volumetric methods, which typically require fewer data and less time to apply, to estimate the CO_2 storage resource potential of a given saline formation or saline system. Both methods were applied to the open-system upper Minnelusa Formation of the PRB, United States, and a closed-system comprising the Qingshankou and Yaojia Formations in the Songliao Basin, China. These saline systems were selected as they represent an open and a closed system, allowing for a better comparison of the volumetric and dynamic approaches. The volumetric methodology and open-system storage efficiency terms described in the DOE Carbon Sequestration Atlas of the United States and Canada (1) and the closed-system efficiency term described by Zhou and others (2) were used to estimate the effective CO_2 storage resource potential and efficiency in both the upper Minnelusa and Qingshankou–Yaojia systems.

Reservoir simulation was used to determine the dynamic CO_2 storage resource potential and efficiency values. In both the volumetric and dynamic approaches, a geocellular model was constructed of the entire storage formation and overlying sealing formations. In both the volumetric and dynamic approaches, the same geologic model was used so that the assessments made could be compared on a consistent basis. For each system, the effective open-system and closed-system storage efficiency terms were calculated so they could be compared to the storage efficiency as determined using the dynamic approach. The volumetric methodology was applied to the two systems, using both the open- and closed-system efficiencies. This resulted in open-system effective CO_2 storage efficiency in the upper Minnelusa Formation of 2.9% to 11% and

closed-system effective CO_2 storage efficiency of 0.54%. In the Qingshankou–Yaojia system, the open-system efficiency was 1.3% to 10% and the closed-system efficiency was 0.21%. This wide range in effective storage efficiency values is due to the large amount of uncertainty in both the geologic and flow properties of the system.

To test whether these two storage systems are open, closed, or semiclosed, dynamic reservoir simulations were performed on each model. A total of 12 simulation cases were run for both the upper Minnelusa and Qingshankou–Yaojia models to investigate the effects of trapping mechanisms, geologic uncertainty, boundary conditions, well configuration, and injection and extraction strategies. In each simulation run, the entire formation extent and overlying formations were included within the models to better understand pressure buildup effects. Initially, injection was simulated for 50 years; then the maximum dynamic storage was estimated by running a few cases with continuous injection for hundreds or thousands of years until the maximum storage potential was reached. Based on the results, the upper Minnelusa Formation behaved as an open system, with dynamic CO_2 storage efficiency ranges of 0.55%–1.7% after 50 years, 2.5%–7.9% after 500 years, and 3.4%–18% after 2000 years of continuous injection in cases without water extraction. These results are in very close agreement with calculated effective volumetric CO_2 storage efficiency and indicate that the use of a volumetric methodology would be applicable in formations that behave in a truly open manner as long as enough time is allowed for CO_2 injection, as shown in the first table below. However, in the first 50 years of injection, these results are on the low side of the volumetric CO_2 storage resource potential, which could have implications for published CO_2 storage estimates made by volumetric methods. In the case of the Qingshankou–Yaojia system, the dynamic approach resulted in storage efficiency ranges of 0.28%–0.40% after 50 years, 0.45%–0.60% after 500 years, and 0.62%–0.72% after 2000 years of continuous injection in cases without water extraction. These results are in very close agreement with the calculated closed-system efficiency values and indicate that the system is closed or semiclosed, as shown in the second table. This supports the use of a volumetric approach for similar systems, as long as closed-system storage efficiency is applied.

Minnelusa System Effective CO_2 Storage Efficiency

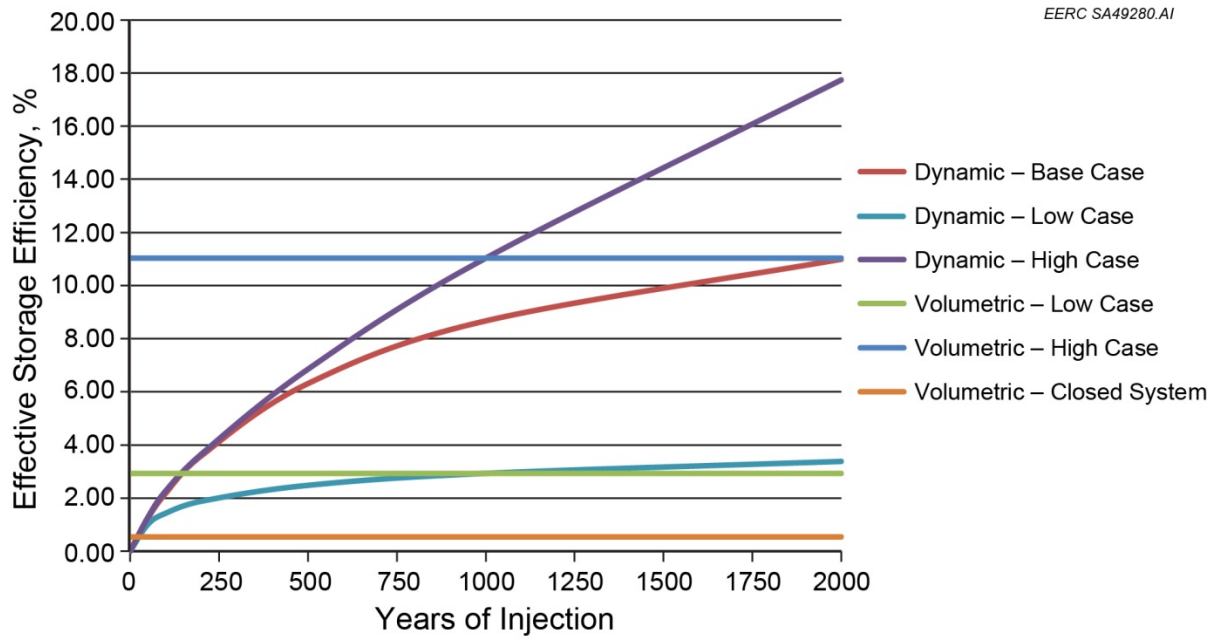
	Low	High
Volumetric Efficiency – Closed System	0.54%	0.54%
Volumetric Efficiency – Open System	2.9%	11%
Dynamic Efficiency – 50 years' Injection	0.55%	1.7%
Dynamic Efficiency – 200 years' Injection	1.9%	4.3%
Dynamic Efficiency – 500 years' Injection	2.5%	7.9%
Dynamic Efficiency – 2000 years' Injection	3.4%	18%

Qingshankou–Yaojia System Effective CO_2 Storage Efficiency

	Low	High
Volumetric Efficiency – Closed System	0.21%	0.21%
Volumetric Efficiency – Open System	1.3%	10%
Dynamic Efficiency – 50 years' Injection	0.28%	0.40%
Dynamic Efficiency – 200 years' Injection	0.39%	0.52%
Dynamic Efficiency – 500 years' Injection	0.45%	0.60%
Dynamic Efficiency – 2000 years' Injection	0.62%	0.72%

This study also investigated the effects of geologic uncertainty, boundary conditions, the number and types of wells used, and water extraction techniques on effective CO_2 storage efficiency. In both the open-system upper Minnelusa and closed-system Qingshankou–Yaojia system, the use of water extraction had the largest effect on CO_2 storage potential, increasing the storage efficiency by as much as 475% in the Qingshankou–Yaojia system and by approximately 100% in the upper Minnelusa Formation after 50 years of operation. The other factors did not play as significant a role in increasing the storage efficiency, as local pressure buildup reduced the rate of injection in the upper Minnelusa Formation and regional pressure buildup was by far the limiting factor in the Qingshankou–Yaojia system.

In open-system cases, the dynamic CO_2 storage resource potential is time-dependent, and it asymptotically approaches the volumetric CO_2 storage resource potential over very long periods of time, as shown in the figure below. This is very similar to other resource industries, namely, the mining and oil and gas industries, where CO_2 is a resource that can only be fully realized if it is exploited to its maximum using advanced technology, notwithstanding time, economics, regulation, and other considerations. In closed systems, the maximum efficiency is reached much more quickly, and the results are roughly equivalent to the volumetric results calculated using a closed-system storage efficiency term. These results indicate that the volumetric assessments can be used as long as an open- or closed-system efficiency term is applied appropriately, with the understanding that the effective CO_2 storage efficiency of a formation will likely take hundreds of wells spaced throughout a formation's area, and it would likely take decades or possibly thousands of years of injection to fully realize the effective CO_2 storage resource potential.



The dynamic CO_2 storage efficiency of open systems is very time-dependent and slowly reaches an asymptote over time that approaches the volumetric effective CO_2 storage efficiency, as shown here with the open-system Minnelusa Formation.

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Subtask 2.18 – Advancing CO_2 Capture Technology: Partnership for CO_2 Capture (PCO_2C) Phase III

Program Areas:	SNESS, CRDP, and CC
Period of Performance:	7/1/13 – 3/31/16
Funding:	DOE: $2,638,321; Nonfederal: $1,362,533; Total: $4,000,854
EERC Subtask Manager:	John Kay
DOE Technical Monitor:	Isaac Aurelio
Nonfederal Partners:	Basin Electric Power Cooperative, Cansolv Technologies, CO_2 Solutions, Korea Carbon Capture and Sequestration R&D Center (KCRC), Montana–Dakota Utilities Co., NDIC, NPPD, PPL Montana, and Tri-Mer Corporation
Final Report:	Kay, J.P.; Azenkeng, A.; Fiala, N.J.; Jensen, M.D.; Laumb, J.D.; Leroux, K.M.; McCollor, D.P.; Stanislowski, J.J.; Tolbert, S.C.; Curran, T.J. *Subtask 2.18 – Advancing CO_2 Capture Technology: Partnership for CO_2 Capture (PCO_2C) Phase III*; Final Report (July 1, 2013 – March 31, 2016) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291 and multiclients; EERC Publication 2016-EERC-03-13; Energy & Environmental Research Center: Grand Forks, ND, March 2016.

Phase III of the PCO_2C Program was conducted under Subtask 2.18, which was initiated under Subtask 2.15. Industries and utilities continue to investigate ways to decrease their carbon footprint as concerns mount about the potential role of CO_2 in global climate change. CCS can enable existing power generation facilities to meet the current national CO_2 reduction goals. Unfortunately, capture is currently expensive and additional research is needed to find ways to decrease the cost. Under PCO_2C, ways to reduce the cost of capturing CO_2 have been sought. Phase III focused on several important areas.

Two flue gas pretreatment technologies that can enhance the performance and reduce the cost of postcombustion CO_2 capture systems were evaluated. First, PCO_2C worked with Cansolv Technologies Inc. to test the operability of a benchmark solvent and an improved formulation for removal of SO_2 from the flue gas. The flue gas extends the life of a CO_2 capture solvent by reducing the formation of heat-stable salts. Both solvents were equally easy to run in the pilot-scale PCO_2C system, although the advanced formulation has a propensity to foam and should always be employed with an antifoaming agent. The testing indicated that the choice of solvent should be made based on both SO_2 removal effectiveness and the energy input required for regeneration rather than on solvent operability.

The second pretreatment technology tested was the Tri-Mer flue gas filtration technology, which combines particulate, NO_x, and SO_2 control. Testing with the Tri-Mer filter system resulted in high levels of capture for particulate, NO_x, and SO_2. NO_x capture and SO_2 capture were highly dependent on temperature, ammonia injection rate, and the amount of sorbent used. Two sorbents produced by Sorbacal, SP and SPS, were used in testing. The SPS material achieved higher levels of SO_2 removal than did the same amount of SP material. The Tri-Mer system was found to be effective for the removal of impurities prior to postcombustion CO_2 capture, although the testing showed that it may be necessary to additionally trim SO_2 levels.

Two new postcombustion capture solvents were tested on the PCO_2C small pilot-scale system. The first solvent tested was from KCRC. Capture rates of 70% to 94% were observed for KCRC's Solvent-B, with steady-state data collected at several different test points. Solvent-B appeared to perform at least as well as 30 wt% MEA. It achieved 90% capture with an approximately 40% lower liquid/gas ratio (L/G) and 30% lower regeneration energy input than MEA at the same capture level.

The second postcombustion capture solvent evaluated was developed by CO_2 Solutions Incorporated. CO_2 Solutions' proprietary technology employs the enzyme carbonic anhydrase as a catalyst within a salt solution. The solvent requires that the stripping column be run at a slight vacuum. Most of the tests were performed with natural gas-derived flue gas, with a few test periods during which solvent performance using coal-derived flue gas was measured. The test campaign showed no degradation in performance of the enzyme catalyst, showed no generation of toxic waste by-products, and demonstrated the ability to use low-grade heat for regeneration, significantly reducing the cost to capture CO_2.

Nine membranes for the separation of hydrogen and CO_2 from coal-derived syngas were provided by Commonwealth Scientific and Industrial Research Organisation (CSIRO) for evaluation as a precombustion CO_2 capture technology. The testing was performed on syngas produced in the EERC's fluidized-bed gasifier using warm-gas cleanup techniques and CSIRO's hydrogen separation membranes. The membranes' performance increased as the temperature increased and was comparable to the performance of other membranes tested at the EERC.

A detailed process-modeling effort was undertaken to develop the basis for determining the cost of CO_2 capture using advanced postcombustion capture technologies and techniques, including the solvents from KCRC and CO_2 Solutions. Partial capture with MEA was also modeled. The models were developed using Aspen Plus® software and mimicked the boiler and steam cycle for Cases 11 and 12 from DOE's baseline study (1). Plant performance for the KCRC solvent is significantly improved over Case 12, which uses MEA solvent. If adequate waste heat can be gathered from the power plant for solvent regeneration and if the CO_2 Solutions solvent performs comparably to MEA, significant increases in overall plant efficiency and reductions in coal feed rate versus Case 12 can be realized. Kinetic and mass transfer limitations were seen to be significantly reduced for 75% partial capture. At 45% overall capture, the parasitic steam load is less than one-half that of 90% overall capture, improving the overall Case 12 plant efficiency from 28.4% to 33.6%.

Three power plants from the region were modeled using the Carnegie Mellon Integrated Environmental Control Model (IECM) to show the effects that the addition of capture would have on specific net power production, water usage, and revenue requirements for various levels of capture. Important findings included that sulfur removal devices must be installed if not already present; space for the capture plant and storage of solvent and reclaimer waste must be available; use of a bypass during partial capture may minimize the size of the capture tower(s), resulting in a reduction of revenue required to operate the capture facility; and power plants in arid areas may find that addition of a cooling tower could minimize water usage. The results reinforced that a one-size-fits-all approach cannot be taken to adding capture to a power plant.

A laboratory test was performed to determine the feasibility of detecting and quantifying any residual amine as well as its degradation products (particularly nitrosamines) that can be potentially emitted to the atmosphere with the stack flue gases. It was found that solutions of alkanolamine solvents containing pure solvent components as well as their degradation products and flue gas species can be monitored using the Fourier transform infrared spectroscopy (FTIR) technique and that FTIR would be amenable to continuous sampling of stack emissions at CO_2 capture facilities.

PCO_2C Program Phase III placed a strong emphasis on the integration of technologies into total systems so that substantial economic and environmental benefit could be realized. The type of information gathered during Phase III is important for utility stakeholders as they determine how to reduce their CO_2 emissions in a carbon-constrained world.

Reference

1. Black, J. *Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 2a*; DOE/2010/1397; Sept 2013.

Subtask 2.19 – Operational Flexibility of CO_2 Transport and Storage

Program Area:	CS
Period of Performance:	2/3/14–12/31/14
Funding:	DOE: $41,442; Nonfederal: $72,153; Total: $113,595
EERC Subtask Manager:	Melanie Jensen
DOE Technical Monitor:	Andrea McNemar
Nonfederal Partner:	IEAGHG
Final Report:	Jensen, M.D.; Schlasner, S.M.; Sorensen, J.A.; Hamling, J.A. *Subtask 2.19 – Operational Flexibility of CO_2 Transport and Storage*; Final Report (Feb 3 – Dec 31, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2014-EERC-12-17; Energy & Environmental Research Center: Grand Forks, ND, Dec 2014.

In Subtask 2.19, basic background information on the topic of operational flexibility of CO_2 transport and storage was gathered from the literature, with the primary focus on compiling real-world lessons learned about flexible operation of CO_2 pipelines and storage from both large-scale field demonstrations and commercial operating experience. Modeling and pilot-scale results of

research in this area were included to illustrate some of the questions that exist relative to operation of CCS projects with variable CO_2 streams. To make the information as useful as possible, cost implications and knowledge gaps that exist relative to transport and storage of variable or intermittent CO_2 streams were identified.

The real-world results were obtained from two sources. The first source consisted of five full-scale, commercial transport–storage projects: Sleipner, Snøhvit, In Salah, Weyburn, and Illinois Basin–Decatur. These scenarios were reviewed to determine the information that is available about CO_2 stream variability/intermittency on operations at these demonstration-scale projects. The five projects all experienced mass flow variability or an interruption in flow. In each case, pipeline and/or injection engineers were able to accommodate any issues that arose. Significant variability in composition has not been an issue at these five sites. The second source of real-world results was telephone interviews conducted with experts in CO_2 pipeline transport, injection, and storage during which commercial anecdotal information was acquired to augment that found during the literature search of the five full-scale projects. The experts represented a range of disciplines and hailed from North America and Europe.

Variability in mass flow rate can cause variations in temperature and pressure within a CO_2 pipeline. Changes in CO_2 composition will also affect how the CO_2 behaves in a pipeline. Modeling results have indicated that the presence of certain impurities may make it difficult to maintain single-phase flow. The presence of impurities changes the physical and transport properties of CO_2 as well as the CO_2 stream hydraulics. Impurities can change other aspects of the pipeline and lead to fracture propagation, corrosion, nonmetallic component deterioration, the formation of hydrates and clathrates, and even a change in the capacity of the pipeline itself. Impurities make it more difficult to model the conditions needed for safe depressurization and operation at transient conditions. The impurity with the most significant effect on transport and injection of CO_2 is water, which can form corrosive carbonic acid or hydrates that can clog the pipeline. Ensuring that a CO_2 stream meets an appropriate quality specification is crucial.

Modeling/simulation and risk assessments that were researched did not provide information about the specific effects of variable CO_2 streams on pipeline health, safety, and environmental performance. Safe operation of CO_2 pipelines begins with a design that establishes source compositions and flow conditions with a safety margin. Most (if not all) CO_2 pipelines in North America are designed with larger diameters and thicker walls than necessary so as to make it possible to transport additional CO_2 should it become available in the future.

Temporary storage and CO_2 pipeline networks/hubs can be useful for controlling the flow in a pipeline or set of pipelines to minimize compositional and/or mass flow rate variations. Temporary storage can consist of fabricated or geologic storage or pipeline packing, which would likely offer limited storage. Networks can consist of a dedicated pipeline linking a single source to a single geologic sink or various combinations of multiple sources and multiple geologic sinks. Multiple sources can offer options for control of the flow in a pipeline system, especially when the sources are of various types. When some of the sources are not producing CO_2, it is likely that others will be, although it will be important to ensure that not all sources on a shared pipeline vary their rate at the same time. Multiple sources can provide an averaging effect for the CO_2 stream composition, provided that they all meet a minimum quality standard.

Intermittent CO_2 flow to an injection site such as for EOR could result in an inconsistency in CO_2 phase behavior within the in-field distribution pipeline system. If not properly managed, changes in reservoir pressure can result in geochemical reactions such as precipitation of minerals (and perhaps asphaltenes, paraffins, and calcite precipitation) or even change the fluid saturation properties of the rock. This could have long-term impacts on key reservoir characteristics such as injectivity and relative permeability. Prior knowledge of the reservoir characteristics and injectate composition can be applied using standard engineering principles to design and operate injection schemes that minimize the negative effects of CO_2 supply intermittency or changes in composition.

There has been concern regarding possible linkage between variability in CO_2 injection rate and induced seismicity. Unless variability produces excessive rates, pressures, volumes, or other conditions, the effect of CO_2 variability upon seismicity is too subtle to identify or predict.

Major findings of the study are that compression and transport of CO_2 for EOR purposes in the United States has shown that impurities are not likely to cause transport problems if CO_2 stream composition standards are maintained and pressures are kept at 10.3 MPa or higher. Cyclic, or otherwise intermittent, CO_2 supplies historically have not impacted in-field distribution pipeline networks, wellbore integrity, or reservoir conditions. The U.S. EOR industry has demonstrated that it is possible to adapt to variability and intermittency in CO_2 supply through flexible operation of the pipeline and geologic storage facility. This CO_2 transport and injection experience represents knowledge that can be applied in future CCS projects. A number of gaps in knowledge were identified that may benefit from future research and development, further enhancing the possibility for widespread application of CCS.

Subtask 2.20 – Bakken CO_2 Storage and Enhanced Recovery Program – Phase II

Program Area:	CS
Period of Performance:	4/1/14–5/31/18
Funding:	DOE: $2,623,558; Nonfederal: $2,623,558; Total: $5,247,116
EERC Subtask Manager:	James Sorensen
DOE Technical Monitor:	Mary Sullivan
Nonfederal Partners:	Baker Hughes, CLR, Computer Modelling Group (CMG), Hess, Marathon Oil, Schlumberger, and XTO Energy
Final Report:	

The Bakken Formation in the Williston Basin is a world-class unconventional tight oil play with oil-in-place estimates in the hundreds of billions of barrels. Matrix permeability in the Bakken is typically on the order of micro- to nanodarcies, and hydraulically induced fractures are necessary to produce oil from the reservoir. Despite the enormous resource, recovery factors are typically low, ranging from 4% to 10%. The Williston Basin also holds world-class lignite coal reserves. Several large lignite coal-fired power plants in North Dakota and Saskatchewan operate within 100 km, or less, of the most oil-productive areas of the Bakken Formation. The juxtaposition of a need to improve the productivity of a world-class oil resource with a desire to manage CO_2 emissions from nearby power plants has led to an interest in the potential to use CO_2 for EOR and associated storage in the Bakken Formation.

From 2012 to 2018, the Bakken CO_2 Storage and Enhanced Recovery Program was conducted. The DOE and industry consortium-funded program was carried out over two phases. Phase I, which ran from 2012 to 2013, used new and existing reservoir characterization and laboratory analytical data coupled with state-of-the-art modeling to examine the viability of injecting CO_2 in the unconventional tight Bakken Formation for simultaneous carbon storage and EOR. The Phase I results suggested that a better understanding of the fundamental mechanisms controlling the interactions between CO_2 and Bakken rock, oil, and other reservoir fluids in these unique, tight formations is necessary to develop accurate assessments of CO_2 storage and EOR potential. To address those knowledge gaps, a series of laboratory-, modeling-, and field-based activities were conducted from 2014 to 2018 under Phase II of the program.

The Phase II lab- and modeling-based studies demonstrate CO_2 can permeate the Bakken matrix, largely through diffusion, to mobilize oil. Those studies also showed that CO_2 will preferentially mobilize lower-molecular-weight hydrocarbons. In 2017, an injection test was conducted in a vertical well completed in the Middle Member of the Bakken. The objectives of the test were to determine the injectivity of an unstimulated Bakken reservoir (i.e., a reservoir that had not been hydraulically fractured) and the ability of injected CO_2 to permeate the matrix and mobilize oil. The test was conducted in a virgin Bakken reservoir. The well completion program did not include the use of hydraulic fracturing and proppant. Upon perforation, the well did not flow to surface, but oil samples were collected from the well before injection. Approximately 99 tons of CO_2 was injected over 4 days. The CO_2 was allowed to soak for 15 days. Reservoir pressure and temperature were monitored during all stages of the test using downhole gauges. During the flowback period, gas composition was monitored, and fluid samples were collected. Preinjection and postinjection oil samples were analyzed for oil composition to determine the molecular weight distribution of the hydrocarbons. Pulsed-neutron logs were also run before and after injection to evaluate the vertical distribution of the CO_2 in the near-wellbore environment.

Injectivity of the unstimulated Middle Bakken matrix was found to be low, with stable CO_2 injection rates between 6 and 12 gallons per minute and bottomhole pressure during continuous injection from 9400 to 9470 psi. During flowback, the well flowed oil to surface briefly, during which time fluid and gas samples were collected. Analyses of the preinjection and postinjection oil samples indicate that the composition of the postinjection oil samples had greater amounts of lower-molecular-weight hydrocarbons than the pretest oils. Interpretation of the results from the field test suggest that although matrix injectivity is low, injected CO_2 can penetrate the Middle Bakken to mobilize oil from the matrix.

The data from the field test have also been used in simulation modeling exercises to gain further understanding of the flow characteristics of CO_2 in unconventional tight oil formations. The simulations indicated that the alternating huff ‘n’ puff approach showed the best performance in terms of EOR. In the best cases, the alternating huff ‘n’ puff scheme was predicted to more than double the oil recovery factor of a well. These results support the conclusions of previous Phase I modeling work that indicate alternating huff ‘n’ puff approaches may be an effective and economical means of implementing CO_2 EOR and associated storage. The modeling efforts also indicated the presence of water in a Bakken reservoir can have serious impacts on the EOR and CO_2 storage potential of a well. The results suggest that mobile water may tend to accumulate in the lower portions of hydraulically induced fractures, which can impede the contact of injected CO_2 with the lower portions of the Bakken reservoir. As the geographic area of production has

expanded, more Bakken wells have been drilled into areas of relatively higher water saturation. The results of these Phase II modeling efforts make an important contribution to furthering the understanding of the role that formation water may have in CO_2 EOR and associated storage.

The Phase II laboratory experimental data and field testing results were applied to develop a refined methodology for estimating the CO_2 storage potential of a tight oil formation, based on the NETL method developed by Goodman and others (2016). This work yielded estimates of the long-term storage of CO_2 in the Bakken using a revised analytical expression informed by laboratory, literature, and simulation data. Application of the refined method indicates that the organic-rich Upper and Lower Bakken shales may have two to three times more storage resource on a kg CO_2/m^3 rock basis than the nonshale Middle Bakken. The storage estimates for the Bakken shale units range from 5.8 to 26.3 kg CO_2/m^3 rock, as compared to the nonshale Middle Bakken storage estimates which ranged from 1.9 to 12.4 kg CO_2/m^3 rock. The Three Forks storage estimates ranged from 5.6 to 19.9 kg CO_2/m^3 rock.

The results of this project provide field-based validation of previous laboratory- and modeling-based studies. They also provide valuable guidance toward the design and execution of future pilot tests in unconventional tight reservoirs. The results also provide insight about how laboratory-, modeling-, and field-based data can be transformed into plausible descriptors of larger-scale field observations, which in turn will yield improved understanding of the potential CO_2 storage resource and EOR opportunities associated with unconventional tight oil reservoirs. The knowledge gained from the Phase II laboratory, modeling, and field-based activities provides new information and data regarding the ability of tight oil-bearing formations to store CO_2 and realize improvements in oil productivity through CO_2 injection.

Task 3.0 – Alternative Fuels

Subtask 3.1 – Electrochemical Hydrogen Production from Coal

Program Area:	CRD
Period of Performance:	7/1/08–9/30/09
Funding:	DOE: $85,000; Nonfederal: NA; Total: $85,000
EERC Subtask Manager:	Donald McCollor
DOE Technical Monitor:	Steven Seachman
Nonfederal Partners:	NA
Final Report:	McCollor, D.P.; Jiang, J. *Subtask 3.1 – Electrochemical Hydrogen Production from Coal*; Final Report (June 25, 2008 – Sept 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-08-01; Energy & Environmental Research Center: Grand Forks, ND, Aug 2009.

Subtask 3.1 was undertaken to demonstrate the feasibility of hydrogen production by coal electrolysis and to determine if at temperatures greater than 100°C, the voltage required can be

reduced closer to the theoretical limit and the rate of reaction of the coal increased to a practical level. The basic reaction is similar to that of water electrolysis, but with theoretical thermodynamic electrical energy required of only 9.5 kcal/mole H_2 and a theoretical driving potential of 0.21V. The remaining energy required comes from the oxidation of the coal.

Production of hydrogen from coal is currently done by gasification. The process requires separation of hydrogen from CO and other impurities as well as significant equipment requirements best suited to large systems, which do not scale down to smaller distributed systems well. An alternative is the production of hydrogen by the electrolysis of coal, the impetus for this study.

A laboratory-scale electrochemical cell able to operate at elevated temperature and pressure was designed and constructed to study the production of hydrogen from coal electrolysis. The cell was found to be prone to problematic leakage due to the need to frequently disassemble for cleaning and recharging. The use of polytetrafluoroethylene (PTFE) ferrules resulted in acceptable sealing. However, their use limited the maximum temperature and pressure attainable to approximately 160°C at 200 psi (1379 kPa). Above 160°C, the PTFE begins to soften and does not securely grip the SS tubing of the cell.

Testing was performed with a Center lignite and an Antelope subbituminous coal in 0.5M H_2SO_4 electrolyte using porous titanium electrodes coated with electroplated platinum. A paste made from the test coal slurried in the sulfuric acid electrolyte and applied directly to the anode was the best means of ensuring contact of the coal with the electrode. Below 80°C, the cell remained open to the atmosphere, allowing the collection and measurement of produced gas in a water trap. Above this temperature, the cell was sealed and gas collected after cooling the cell to ambient temperature. Because of the cell construction, this gas represents that evolved at both cathode and anode.

The interpretation of the gas production results was difficult because of the inferred presence of several possible simultaneous reactions. A further complication was significant hydrogen being produced by the chemical reaction of the SS cell with the electrolyte. This also introduces Fe^{2+} into the system, which can be further oxidized to Fe^{3+}, which then can react with the coal present. Measured Faradaic efficiencies were very low and below those reported in the literature. This may be due to the high concentration of coal at the anode. Although low, the values show a significant increase at higher temperature. No significant difference was found in the reactivity between the Center lignite and the Antelope subbituminous coal tested. Tests of the Center lignite with the addition of 5 wt% calcium sulfate indicated that the added calcium had no catalytic effect and, rather, appeared to inhibit any reaction. The results suggest that the reactivity of actual carbon materials is much lower than a single carbon atom, since breaking C–C bonds may require high energy. The lignite and antelope coal reactivity may be similar to that of actual carbon materials. Under normal conditions, the electrochemical oxidation of coal may occur at potentials more positive than 1.2 V, very close to the standard potential of the oxygen evolution. Therefore, inhibiting the oxygen evolution may be important for the direct electrochemical oxidation of coal to CO_2 in aqueous solution. The test program did not indicate that hydrogen production increased significantly enough at the elevated temperatures to make the process attractive for small-scale

hydrogen generation. In any case, scale-up of the process will face major materials issues in terms of pressure, temperature, and chemical resistance.

Subtask 3.2 – Development of Next-Generation Coal-to-Liquid Catalysts

Program Area:	CRD
Period of Performance:	7/1/08–2/28/10
Funding:	DOE:$85,000; Nonfederal: NA; Total: $85,000
EERC Subtask Manager:	Jason Laumb
DOE Technical Monitor:	Arun Bose
Nonfederal Partners:	NA
Final Report:	Laumb, J.D.; McCollor, D.P.; Downs, J.G. *Subtask 3.2 – Development of Next-Generation Coal-to-Liquid Catalysts*; Final Report (June 25, 2008 – Feb 28, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-02-03; Energy & Environmental Research Center: Grand Forks, ND, Feb 2010.

The objective of Subtask 3.2 was to develop a more sulfur-tolerant Fischer–Tropsch (FT) catalyst and to design a bench-scale catalyst production system that could produce enough catalyst for the entire flue gas flow from a 4-lb/hr gasifier (approximately 10 scfm). The catalyst formulation consisted of four steps: coprecipitation of $FeO(OH)/Fe_2O_3$ and $Cu(OH)_2$, incorporation of silica, potassium impregnation, and calcining.

The initial coprecipitation process employed an aqueous solution containing $Fe(NO_3)_3$ and $Cu(NO_3)_2$ in the desired Fe/Cu ratio for the final catalyst and a second solution containing aqueous NH_3, which were maintained in stirred round-bottom flasks at 83° ± 3°C. Experiments conducted by Dr. Calvin Bartholomew at Brigham Young University (BYU) indicated that a better product could be obtained by using potassium hydroxide instead of aqueous ammonia and slowly adding the Fe/Cu solution and potassium hydroxide solution to an acetate buffer solution in a batch process to maintain better control of pH. The product obtained with this method had promising surface area after calcining; however, the precipitate obtained in the first preparation step was extremely fine and difficult to filter. A modified approach was tested using potassium carbonate solution instead of potassium hydroxide and performing the coprecipitation step at a higher pH so as to produce a more coarse precipitate. No acetate buffer was used, so the pH had to be carefully controlled. Slight modifications to the process design for producing kilogram-sized batches were made to accommodate the modified precipitation method.

The process design was based on the original formulation method for the coprecipitation in a flowing reactor with a planned production of 1 kg of catalyst per run. Two 15-gal closed-head drums holding the Fe/Cu reagent and the base were placed inside open-head 30-gal drums, which served as containment. A third closed-head 30-gal drum served as a deionized water reservoir for mixing the solutions and flushing the system. Two peristaltic pumps were used to introduce the reagent and base to the reactor. The pumps were cross-connected to the water reservoir to allow flushing of the reactor system and for metering water when mixing the chemicals. Counters added

to the pump motor shafts recorded the pump revolutions. Pumping test results showed that total flow could be measured from the total revolutions to within 1.5%. The reagent and base flowed from the pumps through two preheaters to bring their temperatures to the desired 82°C. Temperature was maintained by internal rod heaters and controllers. The reagent and base were mixed in the reactor, which was also heated. A stirrer provided the required mixing. The pump metering the base was manually adjusted to control the pH measured in the reactor. The precipitated product was continuously drained from an overflow outlet near the top of the reactor through a water-cooled heat exchanger for filtering. The washing step, the silication step, and the potassium impregnation step were batch processes carried out in the collection drum.

Subtask 3.3 – Feasibility of Direct Coal Liquefaction in the Modern Economic Climate

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $70,000; Nonfederal: NA; Total: $70,000
EERC Subtask Manager:	Benjamin Oster
DOE Technical Monitor:	John Stipanovich
Nonfederal Partners:	NA
Final Report:	Oster, B.G.; Strege, J.R.; Kurz, M.D.; Snyder, A.C.; Jensen, M.D. *Subtask 3.3 – Feasibility of Direct Coal Liquefaction in the Modern Economic Climate*; Final Report (June 25, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-06-12; Energy & Environmental Research Center: Grand Forks, ND, June 2009.

Subtask 3.3, a study on the feasibility of direct coal liquefaction (DCL), focused on historical DCL efforts in the United States, technical challenges, real-world application, conceptual costing based on literature review, and comparison of CO_2 emissions from a DCL facility to those from an indirect coal liquefaction (ICL) facility. The United States has been conducting DCL research for decades, spurred by the petroleum price disruptions of the early 1970s. Large-scale DCL demonstrations and bench-scale research efforts resulted in an increased knowledge of DCL process operations and led to a better understanding of DCL process chemistry. The largest challenge that currently faces the construction of a DCL facility is capital cost. This literature study found that the major areas where DCL research is still needed are reducing capital costs with improved catalysts, optimizing processes and catalysts for lignite, effectively separating ash from other heavy products, and optimizing refinery processes for coal-derived liquids.

At the time of this study, Shenhua of China was bringing a commercial DCL facility online. That facility estimated a break-even cost of $35–$40/bbl of oil. Conceptual cost data obtained from the literature showed that DCL products from various technologies ranged from $25.54/bbl of crude oil equivalent up to $140/bbl of crude oil equivalent. For comparison, the average cost of petroleum crude oil in 2008 was $93.05, and the average selling price of West Texas Intermediate (WTI) crude oil was projected as $42 for 2009. These cost data support the hypothesis that a DCL facility could be competitive with petroleum and profitable.

The increased concern over the role of CO_2 emissions in global climate change has made CO_2 an important consideration when planning the construction of a coal liquefaction facility. Therefore, this study compared the CO_2 emissions from a DCL process to those of an ICL process. Based on molar carbon balances, DCL can be a much more carbon-efficient process than ICL. In the ICL case study, it was found that 66 mol% of the carbon in the coal is lost as CO_2. These emissions can be reduced to 50% by using a DCL process where a portion of the coal feed is gasified to produce hydrogen. Further CO_2 emission reductions are realized when methane reforming is used as the source of hydrogen. In that case, only 20% of the carbon is lost in the form of CO_2 emissions. Using a CO_2-free source of hydrogen such as wind- or solar-powered water electrolysis would result in a DCL process that only loses about 11% of the carbon in the coal to CO_2 emissions. Stated differently, depending on if the hydrogen for a DCL process comes from coal, natural gas, or renewable sources, a DCL process emits 16%, 46%, and 55% less CO_2, respectively, than an ICL process.

Subtask 3.4 – Fischer–Tropsch Fuels Development

Program Area:	SNESS
Period of Performance:	7/1/08–6/30/12
Funding:	DOE: $1,350,786; Nonfederal: $171,200; Total: $1,521,986
EERC Subtask Managers:	Bruce Folkedahl and Joshua Strege
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	Albemarle and NDIC
Final Report:	Strege, J.R.; Snyder, A.C.; Laumb, J.D.; Stanislowski, J.J.; Swanson, M.L. *Subtask 3.4 – Fischer–Tropsch Fuels Development*; Final Report (July 1, 2008 – June 30, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-06-04; Energy & Environmental Research Center: Grand Forks, ND, June 2012.

In Subtask 3.4, catalysts and processes were developed to improve the technical and economic feasibility of FT synthesis in the United States in order to enhance the nation's overall energy security. FT technology allows the United States to domestically produce liquid fuels from existing coal and biomass resources. Work focused on upstream processes such as gasification and syngas cleanup, on the FT process itself, and on the downstream process of fuel upgrading.

Work under this subtask occurred in two budget periods (BPs). In BP1, a high-pressure fluidized-bed gasifier (HPFBG) was coupled to a small, pilot-scale, packed-bed FT reactor. Two coal types were gasified: a North Dakota lignite and a PRB subbituminous. In addition, three biomass types were cogasified with the coal and gasified straight. The biomass included switchgrass, dried distiller's grains and solubles, and olive pits. Biomass was gasified untreated, leached, and torrefied.

Syngas was cleaned by using hot sorbent beds to remove H_2S and water-cooled quench pots to remove waters and tars. The gasifier was successfully operated on all coal and biomass types.

Biomass pretreatment by leaching helped to prevent ash agglomeration when cofeeding 30% biomass with coal (either subbituminous or lignite), and biomass torrefaction led to higher gasification temperatures. Untreated biomass led to agglomeration, demonstrating that leaching had helped to improve the gasification potential of the biomass. Issues with gasifier operation prevented any clear results as to whether long-term, sustainable gasification of 100% biomass (that is, without coal blending) was feasible on this system.

The packed-bed FT reactor achieved sustained liquid synthesis and temperature control, demonstrating the feasibility of this design for small-scale operation. However, catalyst deactivation was apparent both from reactor operation and product analysis. Laboratory work showed that the catalyst did not perform well under high CO_2 concentrations as seen in the syngas. In the laboratory, the catalyst suffered 80% loss of productivity when feed was switched from an optimum blend of CO and H_2 to simulated syngas containing significant levels of CO_2 and N_2. Light gasifier tars may also have caused coking in the pilot-scale reactor. An attempt to regenerate the catalyst in the pilot-scale reactor had no noticeable impact on catalyst activity.

A process for generating kilogram-scale quantities of pelletized iron-based catalyst was conceived of, constructed, and tested. Although the process was successful, the catalyst was never used in the packed-bed FT reactor. Laboratory testing under BP3 would reveal that this catalyst had very poor mechanical strength and would not be suitable for use in a fixed bed.

Using AspenPlus™ software, a computer-based model was developed that is capable of accurately predicting the gas composition from the gasifier. Early results from laboratory-scale FT synthesis were used to generate equations for predicting the behavior of the packed-bed FT reactor. However, the syngas composition from the gasifier was sufficiently different from the composition used in the laboratory-scale reactor that the model could not accurately predict the distribution of various components in the FT liquids.

The liquid product from the packed-bed FT reactor was upgraded to improve its fuel qualities. Although not required by the BP1 subtask management plan, the aim of the upgrading effort was to generate specification-compliant jet fuel. The product quality was much improved by hydrotreating, but product enhancement did not fully convert the FT product into jet fuel. The effort demonstrated the feasibility of a FT product-upgrading process and also identified key issues to be considered if the goal of upgrading FT liquids is to produce jet fuel.

BP2 was initially proposed as a collaborative effort with Albemarle Corporation, a global catalyst company. Albemarle would provide in-kind cost share to develop FT catalysts specific to syngas from biomass-rich feeds. This proposal was ultimately rescinded by the EERC, and the funding originally set aside for BP2 was reallocated to projects with greater commercial cost share in the form of cash rather than in-kind.

Since BP1 had shown that both CO_2 and light gasifier tars had a negative impact on catalyst performance, BP3 examined catalyst performance when a gas-sweetening system was used. The basic column design was first modeled using ChemCAD® and AspenPlus to determine operating performance under various conditions. The column design was then finalized based on model

results and constructed at the EERC. Lastly, the column was operated using the same HPFBG and FT reactor used in BP1 to see how strong of an effect gas sweetening had on catalyst performance.

The FT catalyst, coal, and operating parameters were nearly identical to those used in BP1 when syngas was only treated by warm-gas sulfur capture and water quench. The results with gas sweetening showed significant improvement in every metric of FT system performance. Carbon monoxide conversion through the FT skid increased by 280% per unit of catalyst; hydrocarbon production increased by 240%; wax collection increased from zero to 20% of the total organic product; and the quality of recovered FT liquids also increased notably as the saturated content increased from 40% to 55% of the liquid organic product. Heavy, saturated hydrocarbons are generally considered more desirable for fuel processing than light, unsaturated hydrocarbons, so the higher production of wax and saturated liquid means that more of the recovered hydrocarbon could be processed into diesel fuel, jet fuel, lubricant, or wax. The FT product quality also held steady during the entire week of operation, whereas the product had become lighter and less saturated over the course of a few days when running with only warm-gas cleanup.

The iron-based catalyst had clearly underperformed with a high CO_2 concentration during BP1. Cobalt-based catalysts might fare better than iron-based catalysts with similar concentrations of CO_2 as long as the H_2/CO ratio of the syngas is acceptable. The EERC produced a suite of cobalt-based FT catalysts to test this theory using bottled gas. The first two catalysts tested showed little if any activity, so ruthenium was added as a modifier. The cobalt catalyst with ruthenium added performed reasonably well. The cobalt-based catalyst showed decreased activity when exposed to simulated syngas, but the decrease in activity was not as severe as had been the case for iron-based catalysts. This result is not conclusive but does suggest that cobalt may be preferable to iron when CO_2 acts to dilute syngas without changing the H_2/CO ratio.

Subtask 3.5 – Catalytic Coal Liquefaction to Produce Transportation Fuels

Program Area:	CRD
Period of Performance:	7/1/09–9/30/10
Funding:	DOE: $80,000; Nonfederal: NA; Total: $80,000
EERC Subtask Manager:	Ramesh Sharma
DOE Technical Monitor:	Jason Hissam
Nonfederal Partners:	NA
Final Report:	Sharma, R.K. *Subtask 3.5 – Catalytic Coal Liquefaction to Produce Transportation Fuel*; Final Report (June 29, 2009 – Sept 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-09-09; Energy & Environmental Research Center: Grand Forks, ND, Jan 2011.

Under Subtask 3.5, catalytic liquefaction of two LRCs was conducted to produce distillate fuel. Direct liquefaction of coals to produce top-quality liquids requires high-severity conditions. Under these conditions, LRCs react too rapidly for the available hydrogen source(s), resulting in the production of retrograde material. In order to overcome this problem, a two-stage liquefaction process was developed to produce transportation fuels from LRCs.

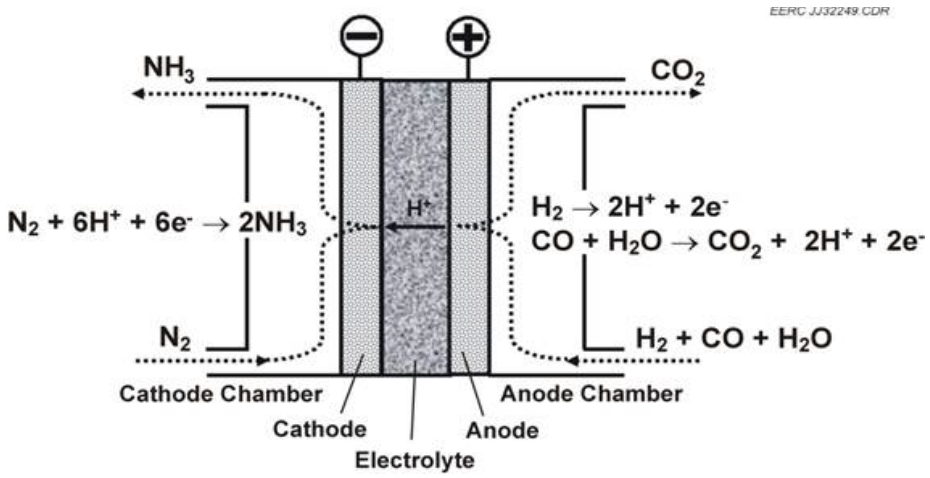
The first stage of the process is a noncatalytic, low-severity liquefaction to mildly process the coal to produce a soluble product. The first-stage liquefaction resulted in ca. 80% (dry, ash-free coal basis) conversion of coal to tetrahydrofuran-soluble product. The first-stage product is then converted into liquid product in the second-stage catalytic high-severity liquefaction. The fractional distillation of the high-severity liquefaction product generated several fractions. The middle distillate (350°–650°F) fraction was fully characterized and upgraded. The upgrading was carried out with an advanced catalyst formulation to produce coal-derived JP-8 blendstocks. The upgraded product was fractionally distilled to produce naphtha, jet fuel, and heavy oil fractions. The detailed mass balance and analyses of each fraction were carried out to determine the fuel properties and overall efficiency of the advanced coal liquefaction process. The jet fraction was fully characterized to evaluate compliance with JP-8 specifications.

The results of this study showed that the fuels meet or exceed most specifications for JP-8. Further research is needed to optimize the upgrading process to produce fuels that meet or exceed the specifications of advanced distillate/jet fuels (JP-8) and produce enough jet fuel for submission to the Air Force Research Laboratory (AFRL) for complete testing.

Subtask 3.6 – Ammonia Production from Electricity, Water, and Nitrogen

Program Area:	CRDP
Period of Performance:	7/1/11–12/31/12
Funding:	DOE: $200,000; Nonfederal: $375,001; Total: $575,001
EERC Subtask Manager:	Ted Aulich
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	Minnesota Corn Growers Association, NDIC, and North Dakota Corn Growers Association
Final Report:	Luo, K.; Aulich, T.R. *Subtask 3.6 – Ammonia Production from Electricity, Water, and Nitrogen*; Final Report (July 1, 2011 – Dec 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-01-01; Energy & Environmental Research Center: Grand Forks, ND, Jan 2013.

Subtask 3.6 was undertaken to develop an electrolytic ammonia synthesis process that uses inputs of electricity, nitrogen, and water or a hydrogen-rich "syngas," a mixture of hydrogen and CO produced via steam reforming of methane or gasification of coal or biomass, as shown in the figure on the top of page 103.



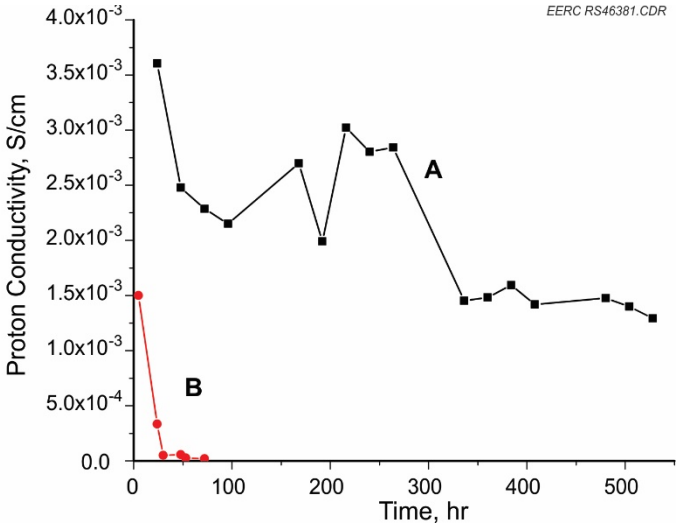
EERC electrolytic ammonia synthesis process.

Unlike Haber–Bosch-based ammonia production processes that use high pressure and temperature (up to 3000 psi and 450°C), the EERC electrolytic process is conducted at ambient pressure and a temperature of 250°–350°C. Because the process is electrically driven and capable of achieving optimal efficiency soon after start-up, it is compatible with intermittent operation, which means it offers potential for use as a power plant load management tool and/or for monetization of wind-generated and other renewable electricity without the need for transmission capacity expansion.

To ensure that the EERC electrolytic process is capable of achieving a commercially relevant ammonia synthesis rate, key requirements are an electrolytic membrane and cathode and anode electrocatalysts capable of sustained operation at a temperature range of 250°–350°C. Because EERC work conducted prior to Subtask 3.6 resulted in development of promising electrocatalysts, the primary focus of Subtask 3.6 was to develop a membrane material capable of meeting the proton conductivity, chemical stability, durability, and other performance requirements at the 250°C minimum process operating temperature.

Following literature review and preliminary laboratory work, a decision was made to focus on development of a polymer–inorganic composite material. Perceived advantages of such a material are an ideal combination of proton conductivity, gas impermeability (critical to ensuring the ability to achieve a seal between anode and cathode), flexibility, and strength that enables meeting performance requirements and lends itself to relatively easy scale-up via commercially available manufacturing techniques. Project activities included 1) design and fabrication of test systems for evaluating membrane materials based on proton conductivity, 2) membrane sample fabrication, 3) evaluation of membrane samples, 4) design and fabrication of 0.2-W membrane–electrode assemblies using best-performing membranes and anode and cathode electrocatalysts, and 5) use of the membrane–electrode assemblies in optimizing ammonia synthesis reaction conditions.

The figure below compares a project-developed polymer-based membrane (A) to a commercially available polymer membrane (B) based on proton conductivity in siemens/ centimeter. The commercial membrane represents one of the highest-temperature-tolerant polymer membranes available, with a maximum recommended operating temperature of about 180°C.



EERC membrane (A) at 300°C vs. commercial membrane (B) at 220°C.

The table below compares EERC-developed membrane–electrode assembly systems on the basis of ammonia production rate in moles/seconds·centimeter^2 (mol·s^{-1}·cm^{-2}) and uses these laboratory-scale data to project commercial-scale electricity consumption (in kWh) and cost for producing 1 ton of ammonia.

Ammonia Synthesis Membrane–Electrode Assembly Performance and Electricity Consumption/Cost

Cathode Catalyst	Potential, V	Temp., °C	Electrolyte Membrane	NH_3 Production Rate, mol·s^{-1}·cm^{-2}	Electricity, kWh/ton NH_3	Electricity Cost, \$/ton NH_3*
Pt/C	2.0	298	Type I	3.41×10^{-11}	1.44×10^{5}	5760
Pt/C	1.8	298	Type I	9.8×10^{-10}	8.34×10^{3}	334
Iron	1.8	260	Type II	1.31×10^{-9}	6.76×10^{3}	272

* Based on electricity cost of \$0.04/kWh.

Using the projected \$272/ton NH_3 electricity cost and adding estimated per-ton-NH_3 production costs of \$132 and \$45 for capital and operating expenses, respectively, equates to a projected cost of \$449/ton NH_3 production. With a 15% increase in process efficiency achievable with moderate improvement to the best-performing membrane–electrode assembly system, the projected production cost decreases to \$370/ton. According to data from the U.S. Department of Agriculture, the U.S. average ammonia price in March 2012 was \$783/ton. Although more work is needed to improve proton conductivity and durability, the project-developed polymer-based membrane has been demonstrated to perform at a significantly higher temperature than its commercially available counterparts and offers the potential for use in ammonia production,

higher-temperature proton exchange membrane fuel cells (with no susceptibility to CO poisoning) and, possibly, other electrochemical applications.

Subtask 3.7 – Beneficiated Lignite Market Study

Program Area:	CRDP
Period of Performance:	8/1/09–6/30/10
Funding:	DOE: $75,150; Nonfederal: $139,855; Total: $215,005
EERC Subtask Manager:	Sheila Hanson
DOE Technical Monitor:	Norman Popkie
Nonfederal Partner:	NDIC
Final Report:	Hanson, S.K.; Azenkeng, A.; Laumb, J.D.; McCollor, D.P.; Pavlish, B.M.; Buckley, T.D.; Botnen, L.S. *Subtask 3.7 – Beneficiated Lignite Market Study*; Final Report (Aug 1, 2009 – June 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-06-09; Energy & Environmental Research Center: Grand Forks, ND, June 2010.

In Subtask 3.7, a study was undertaken to analyze the market for beneficiated North Dakota lignite (BNDL) and identify potential users for market growth. The study consisted of industry and regulatory overviews, a technology review, a transportation analysis, and a market survey and analysis. The results provided vital information about the application of commercial beneficiation processes to North Dakota lignite and the potential market and uses for those products.

BNDL faces a competitive environment as a fuel in an energy arena with many competing products. Within coal markets, BNDL is most directly competing with PRB coal. Aside from coal, the competitive environment includes natural gas, oil, and renewable energy. In 2009, eight new coal-fired power plants with a capacity of 3218 MW became operational in the United States, the largest new coal capacity addition in one year since 1991 (1). However, the coal industry faced challenges, as during that same year, 4605 MW of new capacity was proposed and 14,915 MW was canceled. Out of the 14,915 MW of canceled plants, 65% were not permitted, and 35% were permitted, near construction, or under construction (1). Delays and cancellations were attributed to regulatory uncertainty resulting from climate change and/or strained project economics because of escalated economics in the industry. It should be noted, however, that delayed or abandoned projects still represent future opportunities because the land, fuel, transportation, and water availability still exist.

Emerging clean coal technologies, including CCS and ultrasupercritical boilers, have the potential to enable the installation of new coal-based capacity. In addition, developments in synfuel production, cogasification and polygeneration, and cofiring of coal and biomass present market opportunities for North Dakota lignite or BNDL. Many of the technologies require further development before they can be relied upon as a significant portion of North America's fuel mix.

The regulatory review within the study included renewable energy mandates, climate change and CO_2 impacts, mercury, acid gases, and refined coal tax benefits, along with a review of

technologies available to meet regulatory current and anticipated limits. There is much uncertainty in the regulatory environment, but the expectation with many of the pollutants (trace elements and acid gases) is movement toward a maximum achievable control technology (MACT)-based standard.

If policies to reduce or limit GHG emissions are enacted, that could result in a significant increase in operating costs and reductions in coal use and electrical output by existing power plants and limit the amount of new coal-fired capacity built in the future. The three main options for reducing CO_2 emissions from fossil fuel-based energy systems are 1) increasing the fuel conversion efficiency, 2) switching to a fuel with a lower fossil carbon content, and 3) capturing and storing the CO_2 emitted from the fossil fuel. The first two options are currently not sufficient for reducing CO_2, as the United States relies, and is expected to continue to rely, heavily on coal for energy production.

There are several approaches to upgrading lignite, brown coal, and subbituminous coals, and the technologies for thermal evaporative, thermal nonevaporative, mechanical, and ion exchange were reviewed. Two DOE-sponsored demonstration pilot studies, the Rosebud Syncoal and Encoal projects, were also reviewed. Several commercial-scale processes were also reviewed, including the K-Fuel process developed by Evergreen Energy Inc, the DryFining or Lignite Fuel Enhancement System process developed by GRE Energy and partly sponsored by DOE, and the GTLE process developed by GTL Energy (USA) Ltd. The specifications of the commercially available technologies and products are responding to the fuel characteristics demanded by the market as identified in the market survey.

A market survey was conducted to identify potential users of BNDL within the United States and within a 1000-mile radius of western North Dakota coal deposits. Research focused primarily on potential users in closest proximity to potential raw lignite and BNDL. Surveys were completed with 36 contacts in the following categories: existing and new coal-fired utilities, industrial (e.g., ethanol and concrete manufacturers), institutional (e.g., hospitals and municipal energy systems), coal transportation brokers, and technology consultants and developers. The key question posed to potential users was what a beneficiated lignite product would need to look like in order for them to buy it. There is much interest in BNDL but also significant skepticism that BNDL can perform. The target demanded by industry is a beneficiated lignite product that meets or exceeds the specifications of PRB coal, including heating value, moisture, sulfur, and ash content, as shown in the table below. If beneficiated lignite suppliers can meet those targets at a competitive price, the market will respond favorably. Within the region, there is also a strong “buy local” sentiment.

Characteristics of BNDL

Parameter	NDL	BNDL A*	BNDL B*	BNDL C*	PRB Subbituminous
Moisture, %	36.39	36	27	17	27.52
Heating Value, Btu/lb	6822	7000	8000	9000	8631
Sulfur, %	0.82	0.6	0.5	0.8	0.42
Ash Content, %	7.55	6.5	5.8	7.5	5.69
Product Price, $/ton	12.93	13.27	15.16	17.06	10.52

* Coal specifications for three potential BNDL products.

WorleyParsons and the EERC completed the transportation analysis for BNDL along with biomass cofiring options. Origins include North Dakota mines or BNDL suppliers, including Center, Stanton, Beulah, Underwood, and South Heart. The destinations included large cities in the U.S. Midwest, all with access to further transportation to potential end users. A known coal user in South Dakota was also included in the analysis. The destination cities were Milbank, South Dakota; Fargo, North Dakota; Minneapolis, Minnesota; Duluth, Minnesota; Sioux City, Iowa; Chicago, Illinois; and Kansas City, Missouri. The shipping costs ranged between $8/ton and $103/ton for single shipping units.

BNDL has a competitive transportation advantage over PRB coal for all of the 35 routes considered in the study. Since railroads can base their shipping charges on Btu/lb, a 9000-Btu/lb coal specification was used to represent a typical beneficiated product to obtain the results. Rail is favorable over truck transportation in all cases, although on a case-by-case basis, actual bids may indicate a truck advantage at shorter distances.

Interviewees in the market survey expressed interest in switching to BNDL if it is cost-competitive and does not have detrimental impacts to the plant. However, answering those questions is quite complex and is best analyzed on a case-by-case basis. Decisions, particularly with large utilities, involve the input of multiple staff. Switching fuels impacts the plant in many ways and often requires study to determine the feasibility and costs associated with fuel switching.

Computational modeling provides a representation of the potential plant impacts and economics. Since BNDL has improved properties, it can be economically feasible to switch from PRB or other fuels to BNDL for both small- and large-scale power utilities. This is especially true given that there are additional benefits for using upgraded BNDL, including an increase in overall plant efficiency by about 0.7%–3% (higher heating value [HHV]) and a CO_2 emission reduction by about 6%–33%, depending on the choice of beneficiation technology. Increased plant efficiencies and reduced firing rates also lead to further reductions in NO_x, SO_x, and Hg levels, as well as possible savings from operating and maintenance costs and reduction in the size of downstream pollution control equipment.

Although BNDL faces a challenging competitive environment, there are advantages of beneficiated lignite to provide a basis for market growth for the BNDL industry. BNDL has several competitive advantages to take advantage of market opportunities and deal with the challenges, which include the following:

- Transportation – BNDL has a transportation advantage over PRB coal with markets in the central and eastern United States.

- Buy local – There is strong interest by North Dakota, South Dakota, and Minnesota to buy North Dakota lignite.

- Improved coal properties – The increased heating value, reduced moisture, and improved handleability is favorable.

Market challenges include:

- Overall coal environment – The current coal "moratorium" challenges all coal suppliers.
- Competition with PRB – PRB has an established and strong market presence.
- Renewable energy – The regulatory and market push for renewable energy is a challenge for all fossil-based energy.
- Perception of raw lignite properties – Lignite is known for having a low heating value and high sulfur and ash content.
- Natural gas – Since coal and natural gas are both commodity products, price is the primary driver; however, in a carbon-constrained environment, natural gas is perceived to be cleaner than coal.

Market opportunities include:

- New integrated gasification combined-cycle (IGCC) facilities – BNDL is very suitable fuel for an IGCC plant. A near-term opportunity is the Mesaba Energy project in Taconite, Minnesota.
- Coal-fired facilities – Although much time, effort, and resources are needed at the utility scale, even one end user switching from PRB to BNDL would be very significant to the BNDL industry. Some regional facilities were originally designed for lignite and later switched to PRB, often because of sulfur content difference.
- Niche markets – Small industrial and institutional users in the region are able to switch fuels more easily and rapidly than large utilities.
- CO_2 benefits – Biomass cofiring and blending would provide a CO_2 reduction (depending on the carbon accounting in anticipated CO_2 regulations). In addition, the increased heating value of BNDL would provide an efficiency improvement over raw lignite, resulting in a CO_2 reduction.

BNDL suppliers are encouraged to promote the competitive advantages of BNDL. BNDL needs to overcome existing perceptions of raw lignite. In addition to BNDL suppliers' marketing efforts, an industry marketing and public relations campaign by the lignite industry is advised. BNDL represents a significant market opportunity for the North Dakota lignite industry.

Reference

1. Shuster, E. *Tracking New Coal-Fired Power Plants*; National Energy Technology Laboratory Office of System Analyses and Planning, Jan 8, 2010. www.netl.doe.gov/coal/ refshelf/ncp.pdf (accessed April 2010).

Subtask 3.8 – Analysis of Multiple Pathways for Converting Coal to Liquid Transportation Fuels

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $160,000; Nonfederal: NA; Total: $160,000
EERC Subtask Manager:	Kris Jorgenson
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Jorgenson, K.J.; Sharma, R.K. *Subtask 3.8 – Analysis of Multiple Pathways for Converting Coal to Liquid Transportation Fuels*; Final Report (July 1, 2009 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-08; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

In Subtask 3.8, research was conducted under two separate activities to identify effective methods of converting coal to liquid transportation fuels. Activity 1 was a feasibility study, and Activity 2 was a bench-scale study.

Activity 1—a feasibility study of an indirect coal-to-transportation fuel process—set out to determine the feasibility of a pathway using the CO_2 emissions of a coal-fired power plant along with water and electricity to produce H_2 via an electrolyzer and CO via a reverse water–gas shift (WGS) reactor into a FT system for producing liquid transportation fuels. This pathway would eliminate the need for substantial gas cleanup equipment and thus reduce the overall size of the plant required when compared to a coal gasification pathway.

The process was designed to be as simple as possible in order to keep up-front capital cost to a minimum and also to eliminate, as much as possible, gas cleanup equipment before the FT system. The working fluid of sodium hydroxide made it possible to achieve this simple design, as it acts as both an amine fluid to scrub out the CO_2 from the flue gas and an electrolyte fluid for the electrolyzer. Despite this dual-purpose electrolyte/amine fluid, the capital and operational costs associated with the current state-of-the-art electrolyzers were too great to label this pathway as economically viable. Therefore, the baseline comparison of coal gasification to produce transportation fuels is a more economical pathway. The most troubling finding of this study was that the electrolyzer electrical power requirement was so great that only 22% of the CO_2 emissions could be used to produce liquid fuels. This was unfortunate because the desire was to achieve a carbon-neutral coal-fired power plant while producing both electric power and liquid fuels for consumers. Therefore, this pathway would consume all the produced electric power to reduce the CO_2 emissions by 22% while producing liquid transportation fuels. Because of the poor results for the electroyzer pathway, it was decided to expand this study to compare a natural gas pathway to produce the required hydrogen for the FT system.

The objective of Activity 2—bench-scale analysis of coal- and biomass-to-transportation fuels—was to produce a specification-compliant JP-8 fuel from a mixture of bituminous coal and

biomass or waxes via direct liquefaction. A liquefaction process that combines coal and biomass or waxes to produce transportation fuels that meet key requirements for use by the aviation industry was tested. The process involves coliquefaction of a mixture of coal and biomass-derived oil or waxes in a heavy liquid (solvent), which is also coal-derived. The liquefaction produced a distillate that comprised parraffins, isoparaffins, aromatics, and naphthenes, which are key components needed to meet key properties of aviation fuels.

Activities conducted by the EERC during the tenure of this project consisted of catalytic liquefaction of Illinois No. 6 coal mixed with canola oil, algae oil, or wax to produce distillate fuel. The fuels derived from liquefaction of coal produce fuels that contain aromatics and naphthenes, and the fuels derived from biomass are primarily paraffinic. However, none of these fuels have the key components needed to meet the key properties of aviation fuels. In order to overcome this problem, a liquefaction process that combines coal and biomass was developed to produce transportation fuels. The liquefaction of coal–biomass produces fuel that contains components needed to comply with JP-8 specifications. The fractional distillation of the liquefaction product generated several fractions. The middle distillate (250°–650°F) fraction was fully characterized and upgraded. The upgrading was carried out with an advanced catalyst formulation to produce coal-derived JP-8-compliant fuels. The upgraded products were fractionally distilled to produce naphtha, jet fuel, and heavy oil fractions. The detailed mass balance and analyses of each fraction were carried out to determine the fuel properties and overall efficiency of the advanced coal liquefaction process. The jet fraction was fully characterized to evaluate compliance with JP-8 specifications.

The results show that the fuels meet or exceed most specifications for JP-8. Further research is needed to test this concept in a pilot plant to produce enough jet fuel for submission to the AFRL at Wright–Patterson Air Force Base for complete testing.

Subtask 3.9 – Direct Coal Liquefaction Process Development

Program Area:	SNESS
Period of Performance:	3/1/10–7/31/12
Funding:	DOE: $750,000; Nonfederal: $703,125; Total: $1,453,125
EERC Subtask Manager:	Ted Aulich
DOE Technical Monitor:	Steven Markovich
Nonfederal Partner:	Accelergy
Final Report:	Aulich, T.R.; Sharma, R.K. *Subtask 3.9 – Direct Coal Liquefaction Process Development*; Final Report (March 1, 2010 – July 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-07-06; Energy & Environmental Research Center: Grand Forks, ND, July 2012.

In Subtask 3.9, the EERC undertook a project to design, build, and preliminarily operate a bench-scale DCL system capable of converting pulverized, dried coal to a liquid suitable for upgrading to fuels and/or chemicals. The primary objectives were to finalize the design of a continuous-mode bench-scale DCL reactor system based on a preliminary design developed by

the EERC and Accelergy Corporation, construct and shake down the reactor system, and use the system to initiate production of a jet fuel derived from Illinois No. 6 coal. The ultimate objective was to submit a sample of the jet fuel to AFRL for analysis to assess compliance with key selected fuel property requirements cited in MIL-DTL-83133F, the U.S. military specification for JP-8 jet fuel.

Over the course of the project, EERC design and engineering staff worked with Accelergy-provided design consultants. Activities included improving the overall DCL system design; integrating the design into existing and project-developed EERC facilities and infrastructure; and assessing and developing strategies for mitigating the operational risks associated with the DCL system, which—because system operation necessitates the use of high pressure, high temperature, and hydrogen—were of critical importance to maximizing the safety of the operational staff.

At project initiation, the DCL system was slated for installation in an EERC building anticipated to be an ideal location based on a preliminary engineering estimate of the infrastructure improvements needed to support safe and efficient operation of the DCL system. Key improvements needed included ventilation, fire alarm, fire suppression, and gaseous exhaust combustion/flare systems. Because the actual total cost of making these improvements (based on qualified contractor bids received) was higher than the project budget could support, a new site was needed. Several options were evaluated, including skid-mounting the DCL system and temporarily installing it in a semioutdoor location that would enable seasonal operation only, but none of the options evaluated offered the possibility of meeting fuel production deliverable objectives in accordance with Accelergy's expectations. At the approximate 12-month point of the project, developments in nonrelated EERC projects led to an opening in the EERC National Center for Hydrogen Technology® (NCHT®) building, which is equipped with all necessary DCL project-required infrastructure, and tailoring of the DCL unit layout to accommodate this new space was initiated.

Although the site-selection problem resulted in the need for a project extension, activities associated with developing equipment specifications, soliciting bids for major equipment delivery, ordering system fabrication supplies and equipment, and fabrication of unit operations were ongoing and enabled maintaining project progress and focus throughout the time the DCL system was without a permanent installation site. Fabrication and installation of the DCL system and an accompanying distillation system (for off-line fractionation of raw coal liquids into a naphtha–middle distillate stream for upgrading and a recycle stream) were completed, and shakedown of the system was initiated. In addition to completing fabrication of the DCL system, the project also produced a 500-mL sample of jet fuel derived in part from direct liquefaction of Illinois No. 6 coal and submitted the sample to AFRL for evaluation. The sample was confirmed by AFRL to be in compliance with all U.S. Air Force-prescribed MIL-DTL-83133F-derived alternative aviation fuel initial screening criteria.

Subtask 3.10 – Bench- and Pilot-Scale Evaluation of Processing Conditions and Catalyst for Syngas Conversion to Mixed Alcohol Fuels

Program Area:	CRDP
Period of Performance:	7/1/11–12/31/11
Funding:	DOE: $118,355; Nonfederal: 150,937; Total: $269,292
EERC Subtask Manager:	Ted Aulich
DOE Technical Monitor:	Arun Bose
Nonfederal Partner:	Standard Alcohol Company of America (SACA)
Final Report:	Sharma, R.K. *Subtask 3.10 – Bench- and Pilot-Scale Evaluation of Processing Conditions and Catalyst for Syngas Conversion to Mixed Alcohol Fuels*; Final Report (July 1 – Dec 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-01-01; Energy & Environmental Research Center: Grand Forks, ND, Jan 2012.

The objective of Subtask 3.10 was to optimize and demonstrate a SACA-developed thermocatalytic process to convert synthesis gas to a high ethanol-content mixed-alcohol fuel. The primary project objectives were to 1) conduct a series of bench-scale evaluations of a SACA-provided catalyst and a series of SACA-specified processing conditions for conversion of syngas to mixed alcohols, 2) select a set of optimal processing conditions for use in a small pilot-scale test, and 3) operate the pilot-scale syngas-to-mixed-alcohols process for about 90 hr to evaluate longer-term catalyst performance (using the selected optimal conditions) and overall process viability as well as make larger quantities of product. The objectives were achieved using bench- and pilot-scale reactor systems designed, fabricated, and operated by the EERC, with on-site consultation provided by SACA during both the bench- and pilot-scale testing operations. Process and product data acquired in both online and off-line analytical activities were reduced and evaluated by the EERC and SACA. Key findings included the following:

- Under optimal operating conditions, a product mix of less than 35% methanol and more than 65% higher alcohols—primarily ethanol, with lesser amounts of propanol, butanols, pentanols, and hexanols—was consistently achieved.

- Under certain conditions, a product mix of nonoxygenated hydrocarbons and alcohols was generated. These liquids appeared as two distinct, easily separable phases, both of which could be used as fuels.

- The SACA catalyst did not show any significant loss of activity and selectivity during 150 hr of operation under widely varying conditions, including the addition to the syngas of H_2S and CO_2.

- The bench- and pilot-scale tests yielded information needed for process scale-up and commercialization—in particular, critical information regarding the impact of catalyst density on activity, selectivity, and thermal behavior.

Subtask 3.11 – Production of CBTL-Based Jet Fuels from Biomass-Based Feedstocks and Montana Coal

Program Area:	CRDP
Period of Performance:	2/1/13–6/30/14
Funding:	DOE: $83,333; Nonfederal: $117,187; Total: $200,520
EERC Subtask Manager:	Ramesh Sharma
DOE Technical Monitor:	Steven Markovich
Nonfederal Partner:	Accelergy
Final Report:	Sharma, R.K. *Subtask 3.11 – Production of CBTL-Based Jet Fuels from Biomass-Based Feedstocks and Montana Coal*; Final Report (Feb 1, 2013 – June 30, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2015-EERC-01-23; Energy & Environmental Research Center: Grand Forks, ND, Jan 2015.

Subtask 3.11 was undertaken to modify a recently fabricated DCL system to make it more efficient and user-friendly and use the system to produce 3–5 gal of middle distillate from a Montana coal (Rosebud Mine coal) for submission to the Intertek PARC facility for upgrading. The fractional distillation of the upgraded middle distillate produced a naphthenic fraction with a boiling point distribution similar to petroleum-derived jet fuel.

Rosebud Mine coal was liquefied to produce distillate fuel. The distillate derived from liquefaction of coal produces fuel that contains aromatics and naphthenes, which do not have the key components to meet the key properties of aviation fuels. In order to overcome this problem, the coal-derived fuel was blended with a biomass-derived fuel primarily aliphatic in nature that was obtained from Accelergy Corporation. A blending study demonstrated that equal volumes of coal- and biomass-derived jet fuel along with 11 vol% aromatics needed to enhance its lubricity produced a synthetic fuel capable of compliance with JP-8 specifications. The complete characterization of the composite fuel was performed to determine its compliance with U.S. military specifications for JP-8 jet fuel. Following successful testing of the coal–biomass-to-liquid jet fuel, the fuel was delivered to AFRL for analysis to assess compliance with MIL-DTL-83133F, the U.S. military specification for JP-8 jet fuel.

Subtask 3.12 – Gasification, Warm-Gas Cleanup, and Liquid Fuels Production with Illinois Coal

Program Area:	CRDP
Period of Performance:	9/1/13–6/30/14
Funding:	DOE: $94,230; Nonfederal: $164,062; Total: $258,292
EERC Subtask Manager:	Joshua Stanislowski
DOE Technical Monitor:	David Lyons
Nonfederal Partner:	Illinois Clean Coal Institute (ICCI)
Final Report:	Stanislowski, J.J.; Curran, T.J.; Henderson, A.K. *Subtask 3.12 – Gasification, Warm-Gas Cleanup, and Liquid Fuels Production with Illinois Coal*; Final Report (Sept 1, 2013 – June 30, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2014-EERC-06-27; Energy & Environmental Research Center: Grand Forks, ND, June 2014.

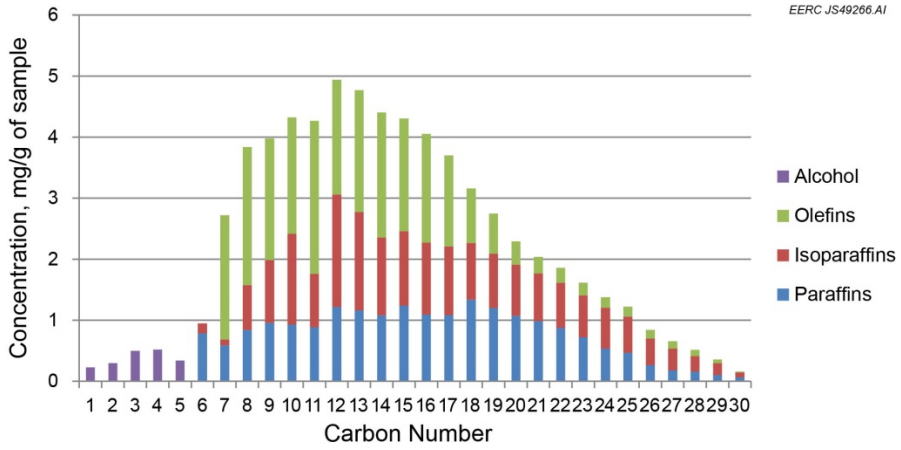
In Subtask 3.12, a project was conducted to demonstrate advanced coal and biomass-to-liquid technologies using Illinois No. 6 coal. The project built on Defense Logistics Agency Energy-sponsored work that was under way with the Connecticut Center for Advanced Technology (CCAT)/Arcadis to evaluate the performance of coal and biomass blends in EERC gasifiers. The Illinois No. 6 coal and biomass for this test program were gasified in the EERC's entrained-flow gasifier (EFG), as high-temperature systems are most suitable for gasification of the selected feedstock. The syngas produced is cleaned using warm-gas cleanup techniques, including hot-gas filtration and fixed-bed desulfurization. The syngas is synthesized into liquid fuel in the EERC's fixed-bed FT reactor. The overall goal of the testing was to determine the impact of warm synthesis gas on the performance and life of a FT catalyst and compare the performance to sweetened syngas.

The EERC has demonstrated the technical feasibility of using coal and biomass blends for liquid fuels production using traditional physical solvents and high-temperature sorbents for gas cleaning. The EERC's small pilot-scale EFG was used to produce syngas from the Illinois No. 6 coal and biomass blends. During testing of FT liquids production, fine particulate matter (PM) was first removed using a particulate collection device, after which bulk sulfur was captured using RVS-1 regenerable sulfur sorbent to remove H_2S and COS to single-digit ppm levels or lower. One RVS-1 bed was used until it became saturated with sulfur, after which the second bed was brought online so that the first could be taken off-line and regenerated. A sulfur-polishing bed was also used after the RVS-1 beds. The WGS beds were not used for this testing. From this point, gas was either sent directly to the FT unit or cooled prior to gas sweetening. For the cold-gas testing, gasifier product water and other condensables were collected and drained in a series of indirectly water cooled quench pots. CO_2 removal and sulfur polishing were achieved using the gas-sweetening adsorption system, a column that uses physical solvent to remove acid gas components from a syngas stream. The gas was then reheated prior to FT liquids production.

Previous testing on the RVS-1 sorbent has shown that it is capable of reliably removing sulfur to single-digit ppm levels in the syngas when PRB coal is gasified. One of the goals for the

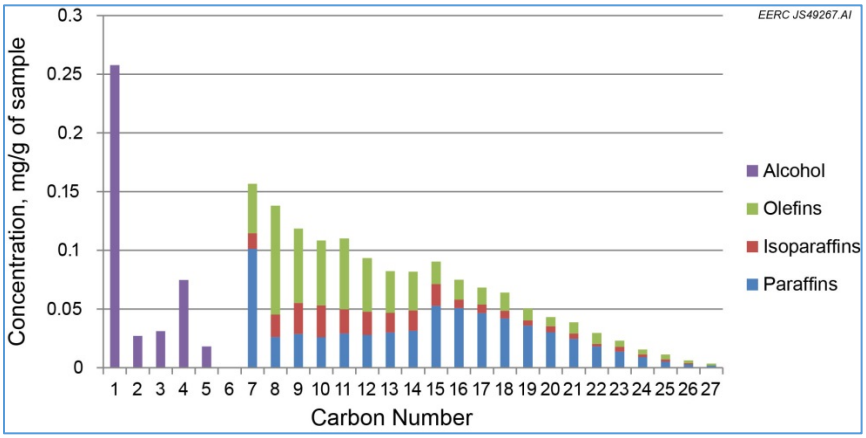
project was to determine if the RVS-1 sorbent was capable of achieving this removal level using Illinois No. 6 coal, which is higher in sulfur. The results indicate that sulfur removal down to 1 ppm or less of H_2S is possible with the RVS-1 and that the beds could be regenerated successfully. Further analysis of the data is under way to determine space velocity requirements and, ultimately, sorbent bed size requirements.

FT liquids were produced during the testing using both warm gas and sweetened gas. The figure below shows the hydrocarbon distribution of the liquids produced using the conventional solvent technology for gas cleanup. The distribution shows that the catalyst is producing higher hydrocarbons with a peak around C13 and that the catalyst is performing reasonably well. It should be noted that the gas-phase catalyst products such as methane are not shown here.



Hydrocarbon distribution of FT liquids produced using sweetened feed gas.

An analysis of samples produced using only the warm-gas cleaning technique is shown in the figure below.



Hydrocarbon distribution of FT liquids produced using warm feed gas.

As can be seen, the hydrocarbon distribution is shifted significantly to the left, and the catalyst is not performing well for the production of FT liquids. These data indicate that the catalyst does not perform well when exposed to CO_2 and moisture, and catalyst productivity is significantly hindered. Overall, the sulfur removal goal of the project was met. The testing successfully demonstrated that sulfur could be removed to below 10 ppm in a single pass using the RVS-1 beds. The second goal of a <20% productivity reduction during the warm-gas testing was met from the standpoint of CO conversion. However, the liquids generated during this testing were not of sufficient quality, and the production of liquid hydrocarbons dropped by more than 20% of the baseline production during the sweetened case.

Task 4.0 – Clean Power Systems

Subtask 4.1 – Feasibility of Hydrothermal Dewatering for the Potential to Reduce CO_2 Emissions and Upgrade Low-Rank Coals

Program Area:	CRD
Period of Performance:	7/1/08–12/31/09
Funding:	DOE: $59,322; Nonfederal: $56,139; Total: $115,461
EERC Subtask Manager:	Brandon Pavlish
DOE Technical Monitor:	Barbara Carney
Nonfederal Partner:	University of Wyoming (through Clean Coal Technologies Research Program)
Final Report:	Azenkeng, A.; Pavlish, B.M.; Lentz, N.B.; Galbreath, K.C.; McCollor, D.P. *Subtask 4.1 – Feasibility of Hydrothermal Dewatering for the Potential to Reduce CO_2 Emissions and Upgrade Low Rank Coals*; Final Report (June 25, 2008 – Dec 31, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-12-09; Energy & Environmental Research Center: Grand Forks, ND, Dec 2009.

Subtask 4.1 comprised an evaluation of the feasibility of hydrothermal dewatering (HTD)/hot-water drying (HWD) for upgrading LRCs and reducing CO_2 emissions. The feasibility of implementing a HWD process for the cobenefit of LRC drying/upgrading and CO_2 reduction was evaluated. A material balance and an economic analysis were performed using information obtained in the literature and bench-scale HWD experiments performed at the EERC. Two PRB subbituminous coals from the Antelope and Buckskin Mines in Wyoming and two lignite coals from the San Miguel and Falkirk Mines in Texas and North Dakota, respectively, were hot-water-dried in a bench-scale (7.6-L) autoclave. To simulate the centrifugation, filtration, hydroclones, and/or flashing methods that are used in commercial- and pilot-scale HWD systems to remove excess water from HWD coal slurries, the bench-scale hot-water-dried coal slurries were air-dried as described in ASTM International (ASTM) Method D 2013, and the proximate, ultimate, and heating value results were reported on an as-determined basis and compared to the untreated coal analysis results on an as-received basis. A summary of the removal efficiencies of moisture, Hg, Cl, O_2, and Na_2O and improvements in heating values resulting from the HWD of Antelope, Buckskin, San Miguel, and Falkirk LRCs is contained in the table on the top of page 117.

HWD Removal Efficiencies and Heating Value Improvements, %

	Antelope	Buckskin[1]	San Miguel	Falkirk
Moisture	30	65	86	64
Heating Value	127	20	45	33
Hg	79	42	2	37
Cl	64	Unavailable	UA	UA
O_2	22	14	2	27
Na_2O	26	>86	<1	61

[1] Average of two HWD treatments.

HWD was effective in removing moisture and increasing the heating value of the four coals. An economic analysis, however, indicates that using HWD for reducing CO_2 emissions from coal is not economically viable given historical carbon credit prices in Europe. If carbon credit prices were to rise and consistently stay in the \$100–\$200 range, then HWD would be a viable technology for CO_2 emission reductions. HWD was also effective in removing Hg, O_2, and Na_2O from most of the coals except the San Miguel coal. Cl was effectively removed from the Antelope coal by HWD. Although not reported, it is anticipated based on the water solubility of chloride minerals that HWD would also be effective in removing Cl from the other coals. Trace element screening analyses (Ni, Al, Be, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Si, V, Zn, As, Ti, Co, and Pb) of process waters from the HWD of Antelope and San Miguel coals indicated that only Ca and Na were present in significant concentrations (≥400 ppm). None of the heavy metals regulated under the Resource Conservation and Recovery Act (RCRA) exceeded the concentration limits established by EPA. The table below indicates the gaseous products from the HWD of coals were predominantly CO_2, O_2, N_2, CH_4, and CO. The San Miguel coal also evolved significant amounts of H_2 and H_2S during HWD.

Composition of Gaseous Products from HWD Coals, mol%

Gaseous Component	Antelope	Buckskin	San Miguel	Falkirk
Hydrogen	0.66	0.58	0.89	0.38
Carbon Dioxide	90.6	86.0	74.1	91.7
Propane	0.10	0.11	0.12	0.05
Propylene	0.12	0.09	0.08	0.06
Isobutane	0.01	<0.01	<0.01	<0.01
N-butane	0.01	0.01	0.01	<0.01
Hydrogen Sulfide	<0.01	0.71	16.5	0.29
1-Butene	0.01	<0.01	<0.01	0.01
Isobutylene	0.02	0.04	0.06	0.02
t-2-Butene	0.01	0.01	0.02	<0.01
Ethylene	0.15	0.13	0.11	0.06
Ethane	0.16	0.18	0.18	0.05
Oxygen	0.71	1.94	1.15	1.24
Nitrogen	2.90	6.65	3.69	3.96
Methane	1.26	1.39	1.71	0.68
Carbon Monoxide	3.29	2.18	1.40	1.53
Total	100.01	99.98	100.00	100.05

Subtask 4.2 – Coal Gasification Short Course

Program Area:	CRD
Period of Performance:	7/1/08–6/30/09
Funding:	DOE: $50,000; Nonfederal: NA; Total: $50,000
EERC Subtask Manager:	Kevin Galbreath
DOE Technical Monitor:	Elaine Everitt
Nonfederal Partners:	NA
Final Report:	Galbreath, K.C. *Subtask 4.2 – Coal Gasification Short Course*; Final Report (July 1, 2008 – June 30, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-06-21; Energy & Environmental Research Center: Grand Forks, ND, June 2009.

In Subtask 4.2, a coal gasification short course was developed to meet the needs of major utilities, independent power producers, and petroleum and chemical companies intent on developing a fleet of gasification plants primarily because of high natural gas prices, the implementation of state carbon standards, and looming federal standards. Projects involving the use of gasification technologies to produce a synthesis gas or fuel gas stream for the production of hydrogen, liquid fuels, chemicals, and electricity are challenging because of the complexity, diverse nature of gasification technologies, and risk associated with certain applications of the technology.

The coal gasification short course consisted of approximately 500 PowerPoint slides designed to provide technical personnel with a broad understanding of gasification technologies and issues, thus mitigating the real or perceived risk associated with the technology. An initial short course was presented September 9 and 10, 2009, at the EERC in Grand Forks, North Dakota.

Subtask 4.3 – Air Quality VII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and Three Preconference Workshops

Program Area:	CRDP
Period of Performance:	7/1/08–1/31/10
Funding:	DOE: $240,000; Nonfederal: $321,081; Total: $561,081
EERC Subtask Manager:	Thomas Erickson
DOE Technical Monitor:	Andrew O'Palko
Nonfederal Partners:	EPRI, event sponsors, and registration dollars from conference and workshop participants
Final Report:	Erickson, T.A.; Fiala, A.M.; Haley, D.J.; Walters, D.A. *Subtask 4.3 – Air Quality VII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and Three Preconference Workshops*; Final Report (July 1, 2008 – January 31, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-01-04; Energy & Environmental Research Center: Grand Forks, ND, Jan 2010.

Under Subtask 4.3, the EERC collaboratively organized and sponsored Air Quality VII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and three preconference workshops. This conference provided participants with strategic information regarding advances made in the topic areas introduced at previous Air Quality Conferences, which reviewed the state of science and policy on airborne pollutants, mainly from utility power generation, and expanded on those issues to address current concerns regarding GHGs and carbon management.

The goal of AQVII was to provide a forum for leaders from industry, government, research institutions, academia, and environmental organizations to discuss key interrelationships between policy and science that are shaping regulations and controls and emerging air quality issues that will lead to acceptable programs and policies to protect human health, the environment, and economic growth. The conference comprised two streams covering carbon management, mercury, and trace substances, allowing participants to discuss and develop proactive responses to breakthroughs, questions, and concerns regarding these airborne pollutants and related issues.

AQVII was held October 26–29, 2009, in Arlington, Virginia. Presentations and discussions addressed the expanded coverage of carbon management, including CO_2 separation and sequestration, and also addressed technology advancements in control methods, including fundamentals/science, sorbent technologies, and scrub/multipollutant systems.

The Air Quality Conference and workshops attracted over 400 participants representing 220 organizations. Attendees represented 38 states, the District of Columbia, and 11 countries (with Canada represented by six provinces). Of those attendees, 66% reported an affiliation with industry, 13% research and academia, 12% government agencies, and the remaining 9% a variety of related areas, including environmental organizations, law, and the media. Keynote speakers at

the conference were the Assistant Administrator of the EPA Office of Air and Radiation, the DOE NETL Director, an API representative, and a U.S. Senator.

Following the keynote presentations, the opening session continued to lay the groundwork of the conference with a panel discussion on "Moving Carbon Capture and Sequestration out of the Laboratory and into the Commercial Marketplace." Over 125 presenters participated in the subsequent technical sessions. Another critical component of Air Quality VII was the exhibit show, which was the largest exhibit to date for the Air Quality Conference series and featured a select group of 31 leading organizations in the air quality sector.

Subtask 4.4 – Intermediate-Temperature Alkaline Methanol Fuel Cell

Program Area:	CRD
Period of Performance:	7/1/09–6/30/10
Funding:	DOE: $90,000; Nonfederal: NA; Total: $90,000
EERC Subtask Manager:	Junhua Jiang
DOE Technical Monitor:	Norman Popkie
Nonfederal Partners:	NA
Final Report:	Jiang, J.; Aulich, T.A. *Subtask 4.4 – Intermediate-Temperature Alkaline Methanol Fuel Cell*; Final Report (July 1, 2009 – June 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-09-05; Energy & Environmental Research Center: Grand Forks, ND, Sept 2010.

Under Subtask 4.4, the capability to conduct FT catalyst testing at a scale consistent with a bench-scale continuous fluid-bed reactor was developed, enabling various vendors to test their FT catalysts on actual coal-derived syngas. The project also developed EERC expertise in issues associated with FT liquid production. A study by Dr. Calvin Bartholomew at BYU is further proof that it is possible to build a single reactor (rather than multiple reactors of different sizes) consisting of three 1-in.-diameter, 10 ft-long tubes to accommodate the anticipated range of catalytic activities and process conditions. However, this single reactor should ideally be designed to operate over a significant range of recycle ratio (e.g., 1–10), temperature (25°–400°C), pressure (10–25 bar), flow rate (1–6 scfm), and cooling duty (0.2–1.5 kW). It should have the flexibility of flowing gas to one, two, or three tubes.

Based on the recommended design specifications provided by BYU while staying within the approved budget, the EERC decided to build a two-fixed-bed reactor system with the capability to add a third reactor at a later time. This system was constructed to be modular and sized such that it can fit into the area around the EERC continuous fluid-bed reactor or also be located in explosion-rated areas such as the gasification tower next to the EERC pilot-scale transport reactor or in the NCHT building high-bay area.

Subtask 4.5 – Syngas Minicombustor: Enabling Trace Metal Analysis in Syngas by Conversion of Oxidized Form

Program Area:	CRD
Period of Performance:	7/1/09–6/30/10
Funding:	DOE: $60,805; Nonfederal: NA; Total: $60,805
EERC Subtask Manager:	Mark Musich
DOE Technical Monitor:	Steven Seachman
Nonfederal Partners:	NA
Final Report:	Musich, M.A.; Laudal, D.A.; Thompson, J.S.; Nyberg, C.M. *Subtask 4.5 – Syngas Minicombustor: Enabling Trace Metal Analysis in Syngas*; Final Report (July 1, 2009 – June 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-06-02; Energy & Environmental Research Center: Grand Forks, ND, June 2010.

Under Subtask 4.5, a prototype miniature combustion system was developed to convert a trace metal-containing syngas into a combustion-derived flue gas and then verify the concentrations of trace metals in the combustion-derived flue gas. The EERC has been investigating the control of mercury, arsenic (as arsine), and selenium (as hydrogen selenide) in actual and simulated coal-derived high-pressure, high-temperature syngas. Previous attempts to employ CMMs or hydride monitors, two-segment STs, EPA M29 impinger trains, and reactive filters for direct analysis of syngas had produced less than favorable outcomes.

The overall objective of the project was to facilitate the methods currently used to measure trace metal concentrations in combustion-derived flue gas for the evaluation of coal-derived syngas. To this end, it was deemed desirable to develop a prototype miniature combustion system to convert a trace metal-containing syngas into a combustion-derived flue gas and to then verify the concentrations of trace metals in the combustion-derived flue gas. A long-term desired outcome would be to couple the combustion system with a continuous multimetal analyzer, e.g., the Cooper Environmental Services (CES) XFM reactive tape analyzer.

The prototype minicombustor designed and built by the EERC was constructed of commercially available fittings, tubing, and ignition system components and was less than 9 in. in length. Two identical minicombustors were tested, with one treated by a surface passivation process to minimize interactions with the arsenic in the syngas. The minicombustor support system included syngas and supplemental gas supply, mercury and arsine vapor sources, gas flow control, a heated enclosure, gas cooling and moisture condensation, and continuous gas analysis.

The minicombustor system integrity was verified by performing nitrogen balance tests. The molar flow of nitrogen in the syngas/supplemental gas/combustion airstream was compared against the nitrogen in the minicombustor flue gas. Good recovery of nitrogen, ranging from nearly 100% to a high of ~104%, was attained. During typical operation at excess air ratios of 190% to as high as 249%, the nominal minicombustor operating temperature ranged from a low of 639°F to a high around 700°F.

A total of 37 batch sampling tests were performed both on the minicombustor flue gas and the uncombusted syngas and supplemental gas mixture. The impact of sulfur on mercury and arsenic analysis results was evaluated by using a supplemental gas consisting of either 100% H_2 or 7000 ppm H_2S in H_2. Batch sampling methods employed for mercury testing included the ST and a modified M29 (MM29). Batch sampling methods employed for combined mercury and arsine testing included the ST and reactive filters, the latter from CES. Mercury data from batch sampling methods were compared against each other and against a Horiba CMM, while arsine (arsenic) data from the batch sampling methods were compared against each other and a Honeywell continuous hydride monitor.

Testing showed the minicombustor had the potential to be used for the conversion of a mercury-laden syngas without significant loss of mercury. Overall, mercury values measured in the syngas–supplemental gas mixture agreed reasonably well with mercury values measured in the minicombustor flue gas. The data indicated that ST and MM29 results were more consistent with CMM results under syngas combustion conditions relative to analysis of the uncombusted syngas–supplemental gas blend. Further, conversion of H_2S to SO_2 during combustion appeared to reduce the negative impact of H_2S on MM29 performance.

During combustion tests, mercury balance (recovery) values, taken as the ratio of batch sample mercury value/CMM mercury value, ranged from 87.6% to 103.9% for STs and 90.4% to 99.5% for MM29 impinger trains. During noncombustion tests with the syngas–supplemental fuel blends, mercury balance (recovery) values ranged from 99.2% to 108.8% for STs and 75.2% to 130.5% for MM29 impinger trains.

However, the use of the minicombustor for determination of arsenic turned out to be a disappointment. Both the ST and CES reactive filter tests showed little recovery of the arsenic oxide during conversion of the syngas–supplemental gas blend in the minicombustor. A preliminary theory suggests that during combustion of the arsine, the arsenic oxide formed as a fine particulate that condensed or impacted on the walls of the minicombustor system. Acid washing and subsequent analysis of the solution confirmed that the majority of the arsenic was retained within the minicombustor.

With respect to its use as a batch sampling method for mercury, ST results appeared to provide more consistent agreement with CMM results relative to the MM29 technique during analysis of the syngas–supplemental gas (H_2 or H_2–H_2S) blends. In contrast, the Hg values obtained via MM29 appeared to be consistently low relative to CMM values when sampling syngas/H_2 and were consistently high when sampling syngas–H_2–H_2S blends. As a consequence of the observed results, ST sampling was selected over MM29 for subsequent mercury/arsine tests.

The use of the ST for dual mercury and arsenic measurement, however, requires further development. When used for mercury analysis alone, the ST is analyzed by a pyrolysis technique. When used for multimetals, the ST is first subjected to digestion by aqua regia followed by cold-vapor atomic absorption (CVAA). Tests showed a consistent trend of lower Hg values obtained by digestion/CVAA, irrespective of testing on minicombustor flue gas or syngas–supplemental gas blends. The values tended to be skewed further with the presence of H_2S. A modification to the sample workup for multimetal analysis showed promise in a separate project.

Although unexpected, the CES reactive filters appeared to show promise as a technique for batch mercury analysis, both with combustion-derived flue gas and the uncombusted syngas–supplemental gas blends. Based on a limited evaluation, STs analyzed by the pyrolysis technique agreed reasonably well with CES reactive filter values. However, as with the MM29, the presence of H_2S appeared to depress the Hg values.

Subtask 4.6 – Systems Engineering Study of Integrating Algae into Coal Combustion and Gasification

Program Area:	CRD
Period of Performance:	7/1/09–6/30/10
Funding:	DOE: $140,000; Nonfederal: NA; Total: $140,000
EERC Subtask Manager:	Chad Wocken
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Zhuang, Y.; Laudal, D.L.; Martin, C.L.; Wocken, C.A. *Subtask 4.6 – System Engineering Study of Integrating Algae into Coal Combustion and Gasification*; Final Report (July 1, 2009 – June 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-06-12; Energy & Environmental Research Center: Grand Forks, ND, June 2010.

Subtask 4.6 comprised a study on integrating algae into coal combustion and gasification processes. An integrated power plant–algae-farming system has been considered as one potentially environmentally and economically sustainable approach that could provide CO_2 avoidance and also generate value-added products to existing industries by producing a "green fuel." Other than a CO_2 stream, a coal-fired power plant can also provide several other potential complementary process streams for large-scale algae cultivation. Water recovered from flue gas, the wet cooling tower, and WFGD can be recycled into an algae system as makeup water to offset water loss in algae cultivation. Rejected thermal energy from the plant steam cycle could be used for algae drying or reactor heating (low grade ~40°C). NO_x and various elements in fly ash can be used as supplemental nutrients for algae growth. Coal ash and FGD lime slurry could be also used as flocculants in algae harvesting.

A case study on an integrated algae–power plant (100-MW_e) was performed, and sensitivity analyses were conducted on different design parameters to identify optimum approaches. Results demonstrated that coal flue gas must be conditioned to ~25°C with less than 50 ppm SO_2. Nutrients possibly recovered from flue gas and coal combustion by-products (CCBs) can only partially meet requirements for algae growth and, subsequently, low-cost nutrient sources should be collocated with the algae–power plant. Energy balance modeling indicates that an open-pond, flat-plate reactor needs substantial supplemental cooling that far exceeds the thermal and water demands of the host power plant, and sealed algae reactors have the performance potential to make integrated algae production a net producer of energy. However, such systems still need development and would currently be expensive for large-scale deployment. Improvements to harvesting technology would dramatically affect the potential net energy balance for power plant–algae reactor

integration. Based on this study, to achieve an economically feasible algae–power plant technology, the following topics of study were recommended in order of importance:

- Decreasing the energy intensity of algae harvesting.
- A low-cost, sealed reactor design capable of convective thermal management.
- A detailed study using CCBs as nutrients or other inputs, e.g., flocculation additive.
- Design solutions for dispersing large-volume flow of ground-source emissions.

Subtask 4.7 – Fluid-Bed Testing of Catalyzed Feedstocks

Program Area:	CRDP
Period of Performance:	3/1/09–10/31/19
Funding:	DOE: $23,513; Nonfederal: $43,604; Total: $67,117
EERC Subtask Manager:	Michael Swanson
DOE Technical Monitor:	Sara Zenner
Nonfederal Partner:	GreatPoint Energy (GPE)
Final Report:	Swanson, M.L.; Musich, M.A. *Subtask 4.7 – Fluidized-Bed Testing of Catalyzed Feedstocks*; Final Report (March 1 – Oct 31, 2009) for U.S. Department of Energy National Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2009-EERC-11-03; Energy & Environmental Research Center, Grand Forks, ND, Nov 2009.

In Subtask 4.7, a small high-pressure fluid-bed reactor was constructed in order to conduct small bench-scale catalytic gasification tests with GPE's new version of the bluegas™ process. GPE's technology employs a novel catalyst to "crack" the carbon bonds to "refine" coal and transform the coal into clean-burning methane (natural gas). This process is called catalytic coal hydromethanation and forms the basis of the GPE bluegas process. In the current version of the process, CO and hydrogen are separated and recycled to the catalytic gasifier to conduct the hydromethanation reactions. Under a new version of the process, pressurized steam and a small amount of oxygen is injected to form the CO–H_2 mixture directly in the gasifier without having to separate and recycle these constituents. The overall goal of Subtask 4.7 was to construct a small high-pressure fluid-bed reactor and to conduct preliminary fluid-bed tests with both a CO–H_2–steam mixture and a dilute O_2–steam mixture fluidizing the bed in order to determine if the use of oxygen affects the activity of the catalyst.

The EERC built a small-batch 1.1-in.-i.d. fluid-bed reactor with an eight-point thermocouple that provided a junction at elevations 0.5, 1, 1.5, 2, 4, 8, 16, and 24 in. above the distributor plate. This close spacing in the bottom of the bed allowed the presence of potential localized "hot spots" to be monitored. This system was designed to operate at pressures as high as 500 psig and temperatures up to 1500°F, with a range of feed gas including steam, nitrogen, carbon monoxide, hydrogen, and oxygen. All tests but one used steam/oxygen injection through the distributor plate, with some nitrogen for pressure tap purges.

Under this project, 26 different tests were conducted on selected GPE feedstocks ranging from uncatalyzed flexicoke to highly concentrated char available from the Gas Technology

Institute testing of the process. Some of the tests had good fluidization even in this small-diameter reactor, resulting in even temperature distributions in the bed. Some of the other tests that did not have good fluidization properties resulted in significant temperature gradients, acting almost like a "cigar burn" through the fluid bed. Analytical testing conducted by GPE showed that the catalyst did not deactivate, even when undergoing almost complete oxidation of the carbon. The fact that the catalyst did not deactivate, even under the worst-case scenarios, suggests that if proper fluidization can be maintained in the gasifier, the use of direct oxygen in the GPE catalytic gasification process should be possible.

Subtask 4.8 – Fate and Control of Mercury and Trace Elements

Program Area:	IEP
Period of Performance:	7/1/09–12/31/11
Funding:	DOE: $3,176,284; Nonfederal: NA; Total: $3,176,284
EERC Subtask Manager:	John Pavlish
DOE Technical Monitor:	Andrew O'Palko
Nonfederal Partners:	NA
Final Report:	Pavlish, J.H.; Lentz, N.B.; Martin, C.L.; Ralston, N.V.C.; Zhuang, Y.; Hamre, L.L. *Subtask 4.8 – Fate and Control of Mercury and Trace Elements*; Final Report (July 1, 2009 – Dec 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-12-09; Energy & Environmental Research Center: Grand Forks, ND, Dec 2011.

Under Subtask 4.8, DOE provided funding to support the EERC's CATM Program, which was established to address current and future environmental issues and the needs of electric and energy production in the United States through research on air toxic metals, in particular mercury. Subtask 4.8 was aimed at developing improved measurement and sampling methods, investigating transformation of metals in energy conversion systems, and developing and testing control technologies that apply to both traditional and advanced combustion systems, with and without CO_2 cocontrol. Efforts were also focused on addressing ongoing environmental concerns related to mercury toxicity and potential impacts of trace metals in the environment. Research outcomes were communicated to regulatory bodies, commerce, government, industrial, and environmental groups as well as educational institutes.

As the United States moves toward the use of advanced energy systems and GHG control and reduction strategies (especially those that involve CO_2 control and sequestration), it is critical that sound scientific research be conducted. To address broad and emerging issues, Subtask 4.8 focused on six activities.

Under Activity 1, management and reporting of all research activities was performed, with direction provided on emerging issues. CATM research is guided by several means, including a Research Advisory Council (RAC) that provides input on research priorities, concepts, and needs as well as feedback regarding emerging issues faced by power generators, industry, and the government. The RAC chair was a representative of DOE NETL.

Under Activity 2, research focused on gaining additional information related to mercury and trace metals in advanced and conventional power systems that target CO_2 reduction. The impact that CO_2 reduction technologies have on mercury behavior and control is unknown, but it is suspected to be significant as process conditions and configurations are significantly different than in conventional power systems. Special emphasis on research within this activity focused on oxycombustion and near-commercial CO_2 control technologies, such as ZGCC and amine-based solvent that can be integrated into existing power systems. Research was performed to validate mercury measurement techniques and establish mercury partitioning in CO_2 control applications. In addition, Hg control technologies were also developed and evaluated in CO_2 control scenarios.

Under Activity 3, the EERC continued to develop and test new and advanced technologies, including sorbents, for mercury and trace element control in power systems equipped with conventional and multipollutant emission control devices. These include power systems with individual or combinations of fabric filters, ESPs, SCR units, wet and dry scrubbers, or other multipollutant technologies that can capture/reduce particulate, NO_x, SO_x, trace elements, etc. The likely issuance of a MACT standard will require that all existing 1200-plus units in the United States now also meet Hg and trace element limits.

Areas that continue to provide challenges to mercury capture in conventional systems are those that either have concentrations of SO_3 that are naturally high because of transformation mechanisms within the system or that use SO_3 injection as a means of flue gas conditioning. Several approaches were pursued to improve the sorbent-based removal of mercury from these systems. A number of novel mercury sorbents were evaluated, and sorbent–mercury modeling was used to optimize performance of sorbent injection systems.

Another area of concern is mercury and trace element capture across systems with WFGD systems. Power plants burning high-sulfur coals are now required to install and operate FGD systems. EPA information collection request (ICR) data suggest that up to 95% mercury capture is possible if these plants are also equipped with SCRs. However, the actual level of capture is highly variable and site-specific, with many plants only able to achieve 60%–70% mercury removal because of insufficient mercury oxidation or reemission of mercury from the FGD slurry. Research focused on improving the retention of mercury in WFGD systems and the resulting impact of these technologies on trace element separation from FGD wastewater.

The final area of emphasis within this activity concerns selenium control in conventional power plants. Selenium is the next most volatile trace element in coal following mercury, and while it is an essential micronutrient for life, selenium can be toxic at elevated concentrations. The liquid-phase release of selenium to the environment is already strictly controlled, and proposed EPA regulations for coal-fired power plants also include surrogate reductions for vapor-phase emissions. Like mercury and other trace elements of concern, the transport and capture of selenium within air pollution control devices is strongly dependent on the specific chemical species and its physical form. Research was conducted to evaluate the reactivity of selenium with conventional mercury sorbents and to consider the role of selenium’s thermophysical properties on capture.

To support the research activities, the EERC evaluated, tested, and developed trace element measurement techniques that can be used in oxycombustion and advanced power systems under

Activity 4. Research Activity 5 focused on addressing trace metal behavior in the environment and the stability of mercury in various natural conditions as well as environmental management of by-products produced from power systems. Research also focused on mercury–selenium interactions, with an emphasis on fish in freshwater lakes. In Activity 6, key research findings were presented and otherwise communicated to regulatory bodies, commerce, government, industry, and environmental groups as well as educational institutions.

Highlights of research outcomes and key findings of Subtask 4.8 include the following:

- Experimental data indicate that mercury measurements with CMMs in flue gas with variable and/or highly concentrated CO_2 may require modifications. Highly concentrated CO_2 streams affect the accuracy of the mass flow rate and subsequent gaseous mercury measurement, although this is specific to the type of CMM used.

- Mercury-sampling data indicate that both CMM and ST methods are capable of providing accurate mercury measurement in a reducing syngas stream, while results of wet-chemistry methods such as EPA M29, show interference from reactions between syngas constituents and reagents used in the wet-chemistry sampling.

- Measurement of trace metals and halogens using M29 and M26a, respectively, is cumbersome and costly. Shipping of hazardous chemicals and samples makes EPA reference methods hard to mobilize in the field. A novel MEST method was developed by CATM that has lower detection limits and uses no hazardous chemicals.

- Mercury enrichment was observed during oxycombustion tests. The total amount of mercury increased and the form changed, implying control implications.

- Other than PM, the emission rates of most HAPs are lower under oxycombustion conditions than those of air-blown combustion.

- Copper-based nanoscale sorbents show reasonable mercury capture in a reducing syngas stream.

- The applied model for calculating in-flight mercury capture with AC was shown to qualitatively predict the limiting factors for mercury capture with a variety of coal flue gases. Furthermore, the insights provided by the sensitivity study of mercury capture result in optimization recommendations that are in agreement with those gained from field experience.

- The inorganic sorbents that were investigated for mercury control in flue gas appear to have reasonable reaction kinetics but far less capacity for mercury capture than AC. Activation methods could be pursued in future work to increase the number of active sites on the sorbent.

- AC sorbents that were investigated because of their extreme physical toughness were found to have poor reactivity and limited active sites. These carbons perhaps may serve as novel catalyst supports but do not appear to be suitable mercury sorbents.

- Additives for preventing the reemission of elemental mercury in wet scrubbers were evaluated for their effect on mercury and selenium precipitation from the scrubber slurry. Their effects on mercury or selenium precipitation were small with a simulated slurry of $CaSO_4$; however, the EERC additive was observed to improve mercury precipitation under basic conditions with a $Ca(OH)_2$ slurry.

- The capture of flue gas selenium across wet scrubbers may be affected by the saturation properties of SeO_2/H_2SeO_3. Measurements of the SeO_2 saturation boundary show that the saturation limits for H_2SeO_3 can be exceeded in FGD systems that quench the flue gas to temperatures below 180°F. This implies that some condensed selenium could slip through wet scrubbers in an analogous manner to SO_3/H_2SO_4.

- Measurements regarding selenium vapor interactions in flue gas suggest that vapor-phase control of selenium may be more difficult than for mercury. Selenium can be captured on AC; however, AC is generally not as efficient for selenium capture as it is for mercury.

- No mercury capture was seen across an amine scrubber used for CO_2 control. Steel coupon corrosion studies showed very little corrosion, with small amounts of MEA and mercury present in a CO_2–water vapor environment.

- While the EPA-approved method to assess leachability of trace elements in coal residuals is comprehensive, it is costly and complicated and requires very skilled personnel to avoid biases. For some residuals, sample conditions could not be maintained as prescribed by the method. The generation of titration pretest pH curves is a labor-intensive process that commonly does not accurately predict the leachate pH behavior of the reactive coal combustion products (CCPs). pH-dependent leaching tests from the leaching framework can provide information over a range of pH values. However, the data must be interpreted with regard to the management of the CCP.

- Mercury emission control strategies can alter the total element concentrations of some elements in the CCPs, specifically arsenic, beryllium, fluoride, lead, manganese, mercury, and selenium. Many of the elements leached less than 5% of the total amount in the CCP. Several elements were not detected in any of the leaching tests performed on individual CCPs. Up to 60% of the total Se and S (measured as sulfate in the leachates) leached from the CCPs. The highest percentage of Se or S leached occurred in the pH range of 8–9.

- Hg can sequester Se, thereby creating the potential for toxicity within organisms. Sufficient data were obtained to posit a model that shows this interaction and the means of the second-order toxicity effect.

- The most important aspects of the seafood and freshwater fish consumption issue involve MeHg binding to Se, the molecular target of MeHg toxicity. Findings indicate that high

MeHg accumulation in fish from certain lakes can result in high Hg:Se molar ratios that approach levels potentially associated with adverse health effects, especially in sensitive subpopulations of consumers. However, the relative percentage of water bodies in the United States that may contain fish that pose such risks appears to be quite low, probably less than 5% and possibly less than 2%.

- As a supplement to a parallel, but separate, project funded by the National Oceanic and Atmospheric Administration, a documentary on the health benefits of eating ocean fish, fact sheets, a brochure, and a Web site were created to supplement information provided in the documentary; this includes data from this project. Information was provided to the United Nations Environmental Programme mercury program on mercury control technologies, which will be distributed worldwide. Research results were presented at numerous venues, and several peer-reviewed papers were published.

Subtask 4.9 – Full-Scale Testing of Sorbent Injection Technology for Mercury Control

Program Area:	IEP
Period of Performance:	8/1/09–5/31/10
Funding:	DOE: $368,040; Nonfederal: $551,562; Total: $919,602
EERC Subtask Manager:	John Pavlish
DOE Technical Monitor:	Andrew O'Palko
Nonfederal Partner:	ENMAX
Final Report:	Pavlish, J.H.; Lentz, N.B.; Kay, J.P.; Hamre, L.L. *Subtask 4.9 – Full-Scale Testing of Sorbent Injection Technology for Mercury Control*; Final Report (Aug 1, 2009 – Feb 28, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; Energy & Environmental Research Center: Grand Forks, ND, May 2010.

Subtask 4.9 was undertaken to evaluate sorbent-based Hg control technologies at a coal-fired power plant in support of the effort to find viable and economical Hg control strategies to meet pending regulations. The primary goal was to identify sorbent-based technology options to meet expected Hg reduction requirements, with an overall removal goal of ≥70%.

The EERC has successfully pilot- and field-tested several sorbent-based technologies that offer potential to achieve the Hg removal goal of ≥70%. Based on these test results, the EERC proposed tests to evaluate potential sorbent-based technologies provided by Grünergy Technologies (Grünergy, formerly known as RLP Energy), a company that commercializes a suite of Hg removal technologies that could potentially meet the sponsor's Hg control objectives. For comparison, tests were also performed with a commercial treated AC, which had been tested extensively at the facility and showed that achieving 70% was challenging.

Tests were performed on a 403-MW unit that burns a high-ash, high-alkaline, relatively low Hg content subbituminous coal. Average coal composition based on belt grab and pulverizer samples is given on a dry basis in the table below. The EERC evaluated a SEA, SF10, and numerous proprietary sorbents provided by Grünergy. SF10 was injected into the furnace and Grünergy's proprietary sorbents were injected ahead of one side of the air heater (AH).

Average Properties of Test Coal, Moisture-Free Basis

	Belt Grab Samples[a,b]		Pulverizer Samples[c,d]	
Parameter	Average	Std. Dev.[e]	Average	Std. Dev.
Hg, ppm	0.047	0.007	0.071	0.012
Total Halogens, ppm	11.483	2.806	13.474	1.300
Proximate Analysis, wt%				
Volatile Matter	29.42	1.14	29.22	0.50
Fixed Carbon	52.25	2.73	49.64	1.20
Ash	18.34	3.61	21.14	1.64
Ultimate Analysis, wt%				
Hydrogen	3.82	0.15	3.66	0.12
Carbon	60.60	3.33	58.60	1.51
Nitrogen	0.78	0.04	0.74	0.04
Sulfur	0.26	0.04	0.23	0.02
Oxygen	16.20	0.49	15.63	0.26
Heating Value, Btu/lb	9780	510	9440	264
Heating Value, kJ/kg	22,748	1186	21,958	614

[a] Based on six coal sample analyses.
[b] Belt grab sample as-received moisture content is 19.42%.
[c] Based on 23 coal sample analyses.
[d] Pulverizer sample as-received moisture content is 11.43%.
[e] Standard deviation.

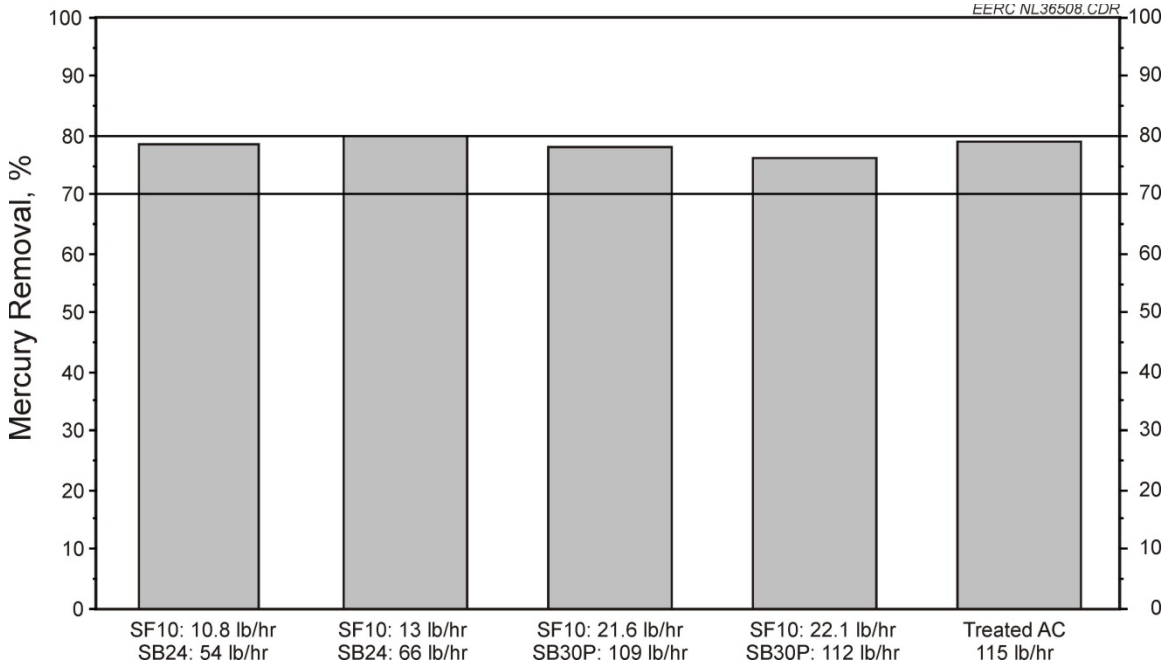
Elemental and total gaseous Hg concentrations were measured with a temporarily installed CMM located at the ESP outlet on the east half of Unit 2. A ST method (similar to EPA M30B) was also used to sample and measure total vapor-phase Hg concentrations periodically at the AH inlet and ESP outlet of the east side of Unit 2. Baseline testing was performed for 3 days to evaluate the variability in flue gas Hg concentrations and the inherent Hg removal performance of the ESP. The average total Hg concentration obtained from ST measurements at the AH inlet was 9.53 µg/dNm^3 at 3% O_2. During baseline testing conditions, average ST data from the AH inlet and ESP outlet indicated an ESP Hg removal efficiency of approximately 25%. Based on Hg in coal concentrations, considering the high variability of Hg in coal, the calculated native removal was slightly higher at approximately 35%, within the range of 25%–35% measured previously.

Parametric tests were performed by injecting SF10 into the burner front of the furnace, with selected sorbents injected at the AH east-side inlet. Several SF10 and sorbent combinations showed promise and were able to easily achieve >70% Hg removal, albeit at varying rates of each material. From these tests, the best two combinations, SF10–SB24 and SF10–SB30P, were selected for extended testing, along with a treated commercial AC for comparison. These combinations exhibited the greatest Hg removal at the smallest injection rates of materials. Following the parametric tests, an extended test of SF10–SB24 was conducted for 5 days, which

was split, with the first half targeted to maintain above 70% Hg removal and the second half to maintain 80% removal. The extended test for SF10–SB30P was interrupted by a plant shutdown to fix a tube leak, but 2 days of testing was completed with a goal of >70% Hg removal and 1 day with a goal of >80% Hg removal.

At the request of the sponsor, two ACs, one plain and one treated, were also tested (without the use of SF10) so that the information could be used to compare this testing with previous test programs carried out on the unit. The target of >70% Hg removal could not be achieved with plain AC. However, testing with the treated commercial AC was successful, and a 2-day extended test was added with this material. The goal of this test targeted a Hg removal of 75%–80% at a constant injection rate based on parametric test results.

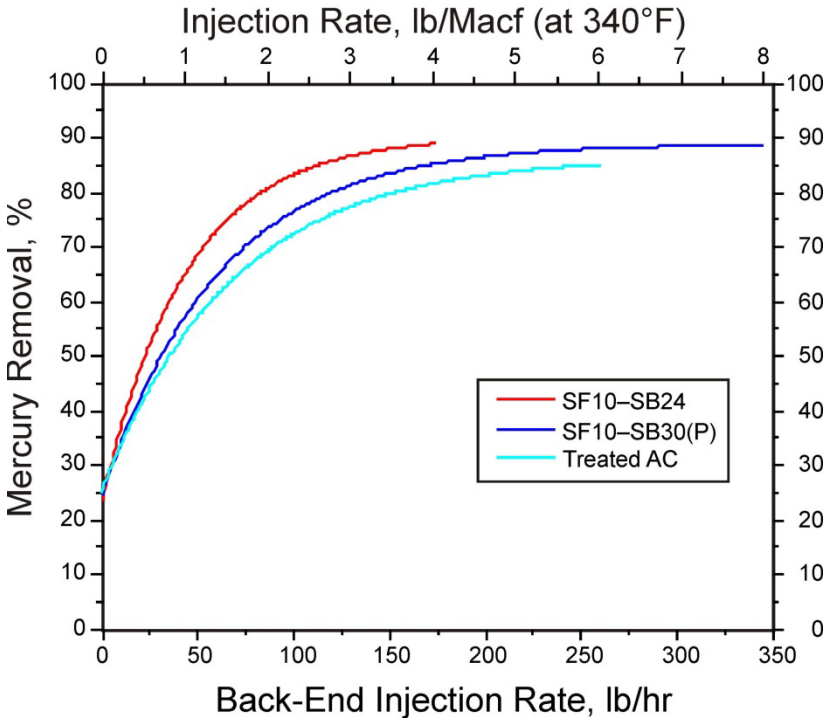
The results of the extended tests, depicted in the figure below, show that all tests surpassed >70% Hg removal and injection rates were slightly higher than needed to maintain that level of removal. The 80% Hg removal target was nearly met (79%), and a slight increase in injection rates would have easily surpassed the goal. The extended tests show that consistent Hg removal can be maintained for an extended period, even as the Hg in coal varied significantly. Maintaining Hg removal of >70% over time at reasonable injection rates appears achievable based on these test results.



Summary of extended test results (note: injection rates shown are for only one-half of the unit).

Sampling of flue gas halogen content showed that although there appeared to be a slight increase in halogen in the ESP outlet gas stream during injection, levels did not exceed 2 ppmv. Coal halogen content was also highly variable, and since a small sampling set of flue gas measurement was obtained, it is not possible to determine with certainty whether this increase was due solely to the injected material or if some of the increase was due to increased concentrations in the coal. Even if it is assumed that all of the increase resulted from the injected material, the

halogen values are extremely low and should not be a point of concern. Dust load sampling at the ESP outlet was conducted in tandem with halogen sampling, and results indicate no increase with the injected materials. Analysis and examination of the ESP hopper ash did not indicate any significant changes. The EERC was successful in presenting several options to the sponsor for controlling Hg emissions beyond 70%, and parametric tests indicated that 90% Hg removal is achievable, albeit at much higher injection rates, with the combination of Grünergy Technologies' additive and sorbents. The figure below summarizes the Hg removal results for the three most promising technologies.



Summary of Hg removal results for the three best technologies. SF10 injection rates are approximately 1/5 the SB24 and SB30(P) rates. The curves are based on data collected during parametric and extended tests. (Note: injection rates shown are for only one-half of the unit.)

The curves represent the parametric and extended test data collected for each technology. Of the three technologies, SF10–SB24 is able to achieve 70%, 80%, and 90% Hg removal at the lowest injection rates. All three technologies were able to achieve the project goal of >70%, with the option for >80% Hg removal. The amount of material for a specific Hg removal appears to be significantly less for the Grünergy Technologies-provided material compared to the commercial treated AC. The materials tested do not appear to introduce unwanted or increased halogen or particulate emissions with their use nor do they alter the composition of the ESP ash. Based on all of the parametric and extended test results, the table on the top of page 133 shows the best approximation of full-unit injection rates required to achieve 70% and 80% Hg removal.

Best Estimate of Injection Rates to Achieve 70% and 80% Mercury Removal for Unit 2

	70% Removal		80% Removal	
Technology	lb/Macf [a]	lb/hr	lb/Macf [a]	lb/hr
Plain AC[b]	–	–	–	–
Treated AC	2.1	178	3.5	300
SF10–SB24	0.3, 1.2	22, 100	0.3, 1.6	26, 140
SF10–SB30P	0.2, 1.2	21.6, 108	0.5, 2.3	40, 200
SF10–SB21	0.3, 1.6	26, 142	0.4, 2.3	34, 198
SF10–SB29	0.4, 2.1	34, 180	0.4, 5.8	34, 500

[a] lb/Macf was calculated with a flow of 1,446,819 acfm at a temperature of 340°F.

[b] 70% and 80% mercury removals were not obtained.

Subtask 4.10 – Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations

Program Area:	IEP
Period of Performance:	1/1/10–6/30/11
Funding:	DOE: $202,316; Nonfederal: $375,765; Total: $578,081
EERC Subtask Manager:	Denny Laudal
DOE Technical Monitor:	Isaac Andrew Aurelio
Nonfederal Partners:	CATM Affiliates Program, EPRI, and ICCI
Final Report:	Laudal, D.L.; Thompson, J.S. *Subtask 4.10 – Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations*; Final Report (March 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291 and Energy & Environmental Research Center; EERC Publication 2011-EERC-06-02; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

Subtask 4.10 comprised an evaluation of the two CMMs most widely used by the utility industry, those manufactured by Tekran and Thermo Fisher Scientific. A number of states, including Illinois, have decided it is necessary to control mercury from coal-fired utilities. In Illinois, essentially 90% removal will be required. Obtaining this level of control will require measuring mercury at concentrations <1.0 µg/m^3. At the time of this study, there were few data in the literature as to the validity of using CMMs to consistently measure mercury at levels <1.0 µg/Nm^3 and no testing done to systematically determine the variability associated with CMMs when measuring mercury at these levels. The only way this could be done was to provide a situation where all aspects of the process were under controlled conditions. Tests were performed at the pilot-scale level, first firing natural gas and using mercury-spiking systems, then completing tests firing coal but in a manner that generated consistently low mercury emissions.

The primary goal of the project was to determine the actual variability of CMMs at mercury concentrations <1.0 µg/Nm^3. To realize this goal, specific objectives of the project were to:

- Determine the uncertainty of the components of the mercury-spiking systems.

- Determine the zero mercury concentration for the instruments.

- Based on "true" spiking values for Hg^0 and $HgCl_2$, determine the variability of the CMMs.

- Compare the variability results with and without acid gases (SO_2 and HCl) added to the flue gas generated firing natural gas.

- Determine the performance of the CMMs measuring low levels of mercury (<1.0 μg/Nm^3) when coal was fired.

To accomplish this goal, pilot-scale tests were conducted, and the accuracy and precision of the instruments were determined by comparing the results to those obtained using a reference method, EPA M30B (mercury ST procedure). The project, therefore, required that the variability of the ST sampling be determined. To assess the precision of the STs, quad train samples were taken. In addition, spiked and blank samples were analyzed.

All of this required a very high level of quality assurance (QA)/QC to ensure that all equipment (the pilot-scale combustor, the mercury-spiking systems, the ST sampling equipment, the Ohio Lumex ST analyzer, and the CMMs) was operating at the highest level—prior to the test, during the test, and at the conclusion of the project.

The overall approach to determining the precision and accuracy of CMMs at mercury concentrations <1.0 μg/Nm^3 was to compare the CMM results to those obtained based on a reference method (EPA M30B). To do this, three primary activities were completed. The first was the initial preparation of the equipment, including the particulate test combustor (PTC), the spiking systems, the CMMs, and the Ohio Lumex. The other two activities were pilot-scale tests. The initial activity was designed to ensure that all the equipment (spiking systems, combustor, ST sampling systems, and Ohio Lumex ST analyzer) was operating at the highest level. The second was to complete 2 weeks of pilot-scale testing firing natural gas and adding mercury using the spiking systems developed at the EERC. Various levels of elemental mercury and mercury(II) chloride were added to the combustor. During the second week, the test was repeated, but this time with HCl and SO_2 added. For each of the test conditions, at least one set of four ST samples were taken simultaneously.

For the third week of testing, an Illinois eastern bituminous coal was fired in the EERC pilot-scale combustor. To reduce the mercury concentration to <1 μg/Nm^3, the flue gas was passed through an ESP, then a high-efficiency fabric filter, and finally a wet lime-based scrubber. Again, at least one set of quad ST samples was taken a day.

At the completion of testing, the data were statistically analyzed to determine the variability associated with the various parts of the process and to determine the true lower limit of quantification for each of the CMMs.

In comparison to multiple ST samples, both instruments performed very well when natural gas was fired. However, the Tekran instrument provided a lower detection limit compared to the Thermo Scientific instrument, 0.01 μg/Nm^3 compared to 0.04 μg/Nm^3 for the Thermo Scientific

CMM. When coal was fired in the pilot-scale combustor, the Thermo Scientific CMM results had a considerable bias. Because of the results firing coal, the correlation with the ST (r^2) was only 0.745 for the Thermo Scientific CMM compared to the Tekran CMM which had an r^2 correlation of 0.990. Because of the relatively poor results when coal was fired, after doing an evaluation of the instrument, ThermoScientific repeated the coal tests. The results for the second test were considerably better, resulting in an overall r^2 value of 0.911.

Subtask 4.11 – Testing of Modified Activated Carbon for Use in Hydrogen and Energy Storage

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $108,000; Nonfederal: NA; Total: $108,000
EERC Subtask Manager:	John Hurley
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Hurley, J.P. *Subtask 4.11 – Testing of Modified Activated Carbon for Use in Hydrogen and Energy Storage*; Final Report (July 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-21; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

In previous work, the EERC developed a treatment method for increasing the electrical conductivity of AC by a factor of 10. The goal of Subtask 4.11 was to further modify the surface of the high-conductivity AC with three different types of treatments (A, B, and C) and then determine the effects of these treatments on the ability of the ACs to store hydrogen or perform as electrodes in electrochemical capacitor and lithium-ion battery energy storage systems. A granular AC was used in the hydrogen storage testing, and two powdered ACs were tested for use as electrodes.

AC does not adsorb hydrogen very well except at low temperatures. However, recent literature has shown that by adding platinum to the AC surfaces, hydrogen molecules are broken into atoms that then can be physisorbed in high concentrations on the carbon surfaces at room temperature, possibly in pores too small to be quantified by typical methods (1–14). Because the surface treatments are known to affect the electrical conductivity of the AC, it was thought that the surface treatments may also affect the ability of the ACs to adsorb hydrogen at room temperature. This activity also includes the work done on treating the AC powders.

Measurements of the amount of hydrogen that could be adsorbed by the carbon showed that if the vessel were completely filled with the variously treated ACs, with and without platinum, the amount of hydrogen that could be stored in a vessel would only increase by between 5% and 23% over the amount of hydrogen that can be stored in an empty vessel at 1000 psig and room temperature. The AC itself can adsorb approximately 0.40% of its weight in hydrogen at 1000 psig and room temperature. Adding 2% platinum by weight increased the hydrogen adsorption to only 0.55%, a 38% relative increase, but still far too little to make the material of value in hydrogen

storage. Similar results were measured for each of the surface-treated ACs both with and without platinum, i.e., very little actual increase in the amount of hydrogen stored and no appreciable effect of the surface treatments on actual hydrogen adsorptivity at 1000 psig and room temperature.

Two kinds of AC materials, labeled as treated Supra 50 and treated PCB-P, respectively, were tested for use as the electrode in both the symmetric ultracapacitors and the lithium-ion batteries. The ultracapacitor testing showed that the Supra 50 enhanced with Treatment A presents the best overall electrochemical performances with high specific capacitance (120 F/g) and superior stability (long cycling life) in a basic electrolyte system. Treatment A did not adversely affect the capacitance of the carbon, but greatly improved the electrode's electrochemical stability, essentially doubling its lifetime, although at a cost of a reduced specific power. The possible reason for the better stability in the cycling test was suggested to be its greatly improved conductivity, which means lower resistance for the flow of current and, hence, less heat generation during cycling. It might have also affected the interfacial chemistry between the electrode and electrolyte which was not covered in this study. This stability improvement as a capacitor electrode is of great economic value.

In the tests of the treated ACs for use in lithium-ion batteries, Treatment C was shown to substantially increase electrode cycle life and capacity retention under high charge and discharge rates. The Treatment C Supra 50 and treated PCB-P both surpass the commercial graphite anode in a test of fast cycling at 100 mA/g regarding its capacity retention and cycle lives. Moreover, the tested modified AC anodes consist of simpler composition (only AC and binder), which means simpler electrochemistry and dynamics, and might help to achieve a more stabilized surface layer, hence contributing to a longer cycle life. This property is valuable in developing high-power energy storage devices to meet the increasing need for fast-charging capability mobile energy storage purposes.

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Subtask 4.12 – Algae Harvesting in an Integrated Power Plant–Algae System

Program Area:	CRD
Period of Performance:	7/1/10–6/30/11
Funding:	DOE: $100,000; Nonfederal: NA; Total: $100,000
EERC Subtask Manager:	Ye Zhuang
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Zhuang, Y. *Subtask 4.12 – Algae Harvesting in an Integrated Power Plant – Algae System*; Final Report (July 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-24; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

In Subtask 4.12, work continued to enhance an EERC-developed electroflocculation method for harvesting algae. An integrated power plant–algae farming system is one potential environmentally and economically sustainable approach to providing CO_2 avoidance while also producing valuable renewable feedstock. Among the various challenges of the integrated power plant–algae concept is algae harvesting/dewatering, which consumes enormous amounts of energy using current commercial technology. Traditional harvesting methods employed in this area are centrifugation, flocculation, and a few other proprietary or adapted technologies. The EERC has developed an inexpensive electroflocculation method to harvest dilute algae from growth medium for downstream processing. This alternative method requires less energy than centrifugation and less chemicals than employed in flocculation. In previous work, a literature study was undertaken on algae charges and separation using electrophoresis. A multiphysics model was set up accordingly to characterize electrokinetic transportation of algae under an electric field. A flat-plate photobioreactor was built to grow algae for harvesting, and the algae strains will be provided by two commercial algae companies.

In this project, the EERC used electroflocculation to concentrate algae cells from 0.2% to 0.5% up to 12% with a low energy input. By applying electricity with controlled voltage and current, selected metal ions were discharged into the algae cultivation medium where the ions neutralized the suspended algae cells that inherently carry negative charges. As a result, the neutralized algae cells formed an agglomerate and settled out because of gravity. The resulting algae agglomerate slurry will be filtered through a metallic membrane with ~20-µm pore size to further concentrate the algae to the levels required by the following liquefaction process. Because of the much-reduced solution volume of the algae agglomerate and the superior cleaning ability of the metallic membrane, the overall energy consumption of the filtration is maintained at a minimum level.

Subtask 4.13 – Full-Scale Mercury Control Demonstration: ICR Sampling with Mercury

Program Area:	IEP
Period of Performance:	8/1/11–6/30/12
Funding:	DOE: $500,000; Nonfederal: $148,800; Total: $648,800
EERC Subtask Manager:	Jason Laumb
DOE Technical Monitor:	Andrew Jones
Nonfederal Partner:	Minnesota Power
Final Report:	Laumb, J.D.; Laudal, D.L.; Schulz, R.L.; Pavlish, J.H. *Subtask 4.13 – Full-Scale Mercury Control Demonstrations: ICR Sampling with Mercury Control*; Final Report (Aug 1, 2011 – June 30, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-06-01; Energy & Environmental Research Center: Grand Forks, ND, June 2012.

Subtask 4.13 was undertaken in response to the EPA-promulgated NESHAPs for the utility industry. Under Section 112 of the CAA Amendments, NESHAPs require MACT for mercury, HCl, and PM as a surrogate for trace elements. Some of the units identified by EPA have the capability for AC injection. However, this still may not adequately represent what impact mercury control would have on the level of HAPs. The EERC's work in this subtask focused on determining the impact of a mercury control technology while sampling for those HAPs that are part of NESHAPs, including mercury, halogens, and trace elements.

The testing was conducted at Minnesota Power's Laskin Energy Center. The testing involved injecting various levels of two sorbents directly into a wet particulate scrubber. The primary objectives of the project were to determine the level of mercury control that could be attained using a proprietary sorbent and a BAC, then determine the impact these materials had on trace metal and halogen emissions.

The results of particulate sampling showed the average particulate removal across the wet particulate scrubber was >99.5%. The removal was not impacted by the addition of either mercury sorbent.

The first objective was to determine the baseline mercury removal (no sorbent). The average baseline mercury concentration at the economizer inlet was 6.78 µg/Nm^3. At the particulate scrubber outlet, the average baseline mercury concentration at the particulate scrubber outlet location was 6.42 µg/Nm^3, resulting in a baseline mercury capture of 5.3%. The average mercury removal appeared to be ~20%–25% with the proprietary sorbent. When the BAC was injected prior to the wet particulate scrubber, the mercury removal was highly dependent on add rate. The maximum mercury removal achieved was 66.4% at an add rate of 13 lb/Macf.

Three coal samples were collected and the chlorides measured. The concentrations were very low: 12.9, 11.5, and 12.7 ppm, resulting in a flue gas concentration of <0.2 ppm. All measurements were below the detection limit. As would be expected, any halogens present in the flue gas prior

to the particulate scrubber were removed, and all were less than the method detection limit. There were no differences as a function of sorbent injection.

Flue gas trace element sampling was performed, and the samples were analyzed for the 11 trace elements listed in the utility NESHAPs. Based on these measurements, with the exception of mercury and selenium, a very high percentage of each trace element (>95%) was removed across the particulate scrubber.

To complete a mass balance for each trace element, in addition to the coal and flue gas samples, the slurries associated with the wet particulate scrubber were sampled. Two trace element balances were completed. The first (Balance 1) was based on the coal trace element concentrations and those measured in the flue gas at the economizer. The second mass balance was around the entire system (Balance 2). The results of these mass balances, with the exception of selenium and nickel, were actually quite good (±20%). In general, the mass balances were quite good, but as expected, the trace element balances completed around the Unit 2 particulate scrubber were more variable. The variability almost certainly was the result of the inaccuracy of the assumptions that were made as well as the process measurements that were used in the calculations.

Based on the results of the testing conducted by the EERC at Laskin Energy Center, the following conclusions can be drawn:

- Overall, particulate removal was quite high for the particulate scrubber. The average removal was 99.57%, and the addition of the two sorbents did not appear to have any impact on particulate emissions.

- Halogen emissions (chlorine, bromine, fluorine) were less than the EERC detection limits of 0.1 mg/L, or 0.8 ppmv), in the flue gas. The addition of BAC had no effect on the halogen concentrations in the flue gas.

- There was little baseline mercury removal across the wet particulate scrubber (average of 5.3%). Mercury removal across the particulate scrubber using the proprietary sorbent ranged from 13.7% to 28.9% but appeared to be independent of add rate. Mercury removal across the particulate scrubber injecting the BAC sorbent ranged from 33.2% to 63.4%, depending on add rate.

- Reasonable mass balances were attained for the 11 trace elements measured. However, a number of assumptions were made.

- As expected, the removal of trace elements across the wet particulate scrubber is very high, >90%, for all three elements, with the exception of mercury and selenium.

Subtask 4.14 – Air Quality VIII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and Preconference Workshops

Program Area:	CRDP
Period of Performance:	6/1/10–4/30/12
Funding:	DOE: $255,000; Nonfederal: $267,856; Total: $522,856
EERC Subtask Manager:	Thomas Erickson
DOE Technical Monitor:	Andrew O'Palko
Nonfederal Partner:	EPRI, event sponsors, and registration dollars from conference and workshop participants
Final Report:	Fiala, A.M.; Erickson, T.A.; Haley, D.J. *Subtask 4.14 – Air Quality VIII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter and Preconference Workshops*; Final Report (June 1, 2010 – April 30, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-04-01; Energy & Environmental Research Center: Grand Forks, ND, April 2012.

Under Subtask 4.14, the EERC collaboratively organized and sponsored Air Quality VIII: An International Conference on Carbon Management, Mercury, Trace Substances, SO_x, NO_x, and Particulate Matter (AQVIII) and Preconference Workshops. This eighth Air Quality Conference provided participants with strategic information regarding advances made in the topic areas introduced at previous Air Quality Conferences, which reviewed the state of science and policy on airborne pollutants, along with issues regarding carbon management. The conference topics focused primarily on challenges and opportunities as they relate to the utility power generation sector. The EERC also organized and conducted two Preconference Workshops: one focused on carbon management and the second on measurement and control of mercury, trace metals, and halogens.

The goal of AQVIII was to provide a forum for leading representatives from industry, government, research institutions, academia, and environmental organizations to discuss key interrelationships between policy and science that are shaping near-term regulations and controls and to further discuss emerging air quality issues that will lead to acceptable programs and policies to protect human health, the environment, and economic growth. The conference comprised two streams of discussion to cover the main topic areas of carbon management, mercury, and trace substances, allowing participants to discuss and develop proactive responses to breakthroughs, questions, and concerns regarding these airborne pollutants and related issues.

AQVIII was held October 24–27, 2011, in Arlington, Virginia, with over 400 participants representing 204 organizations. Attendees represented 39 states, the District of Columbia, and 18 countries (with Canada represented by four provinces). Of those attendees, 58% reported an affiliation with industry, 14% research and academia, 12% government agencies, and 8%

consultants, with the remaining 8% of attendees representing a variety of related areas including environmental organizations, law, and the media.

AQVIII featured an esteemed group of high-level keynote, oral, and poster presenters from around the world who addressed an array of issues regarding air quality. Keynote presenters included U.S. Senators, the Assistant Administrator of the EPA Office of Air and Radiation, the Chief Operating Officer of DOE's Office of Fossil Energy, and the DOE NETL Director.

The conference also featured an opening forum on New Energy Technologies – Development and Implementation Challenges. Participants included EERC, EPRI, and other high-level industry representatives. Another critical component of AQVIII was the sold-out exhibit show, which was the largest exhibit to date for the Air Quality Conference series and featured a select group of 35 leading organizations in the air quality sector.

Subtask 4.15 – Performance of Eskom Coal in a Circulating Fluidized-Bed Combustor

Program Area:	CRDP
Period of Performance:	5/1/10–12/31/10
Funding:	DOE: $50,047; Nonfederal: $93,912; Total: $143,959
EERC Subtask Manager:	Douglas Hajicek
DOE Technical Monitor:	Meghan Napoli
Nonfederal Partner:	Eskom Holdings Limited
Final Report:	Hajicek, D.R.; Henderson, A.K. *Subtask 4.15 – Circulating Fluidized-Bed Combustion Testing of Eskom Coal*; Final Report (March 15 – Dec 31, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-12-02; Energy & Environmental Research Center: Grand Forks, ND, Dec 2010.

In Subtask 4.15, test program was conducted on South African coal and limestone in a circulating fluidized-bed combustion (CFBC) pilot-scale facility at the EERC. Coal and limestone used for this test was shipped from South Africa in super sacks. The coal has a heating value of 19.55 MJ/kg as-received, ash content of 28.9%, moisture content of 5.7%, and sulfur content of 0.8%. The coal ash had 54.4% silica, 30.4% aluminum, with only 3.8% calcium available for sulfur capture. The coal was crushed to a top size of −7000 μm (−0.28 in.) with a d50 of 1500 μm (0.06 in.). The limestone was crushed to −1500 μm, with a d50 of 180 μm. Three test periods were conducted, the first for the evaluation of the inherent sulfur capture with this coal, the second maintained the same conditions while adding limestone at a calcium/sulfur ratio of approximately 1.0, and the third was at a calcium/sulfur ratio of approximately 2.0.

Prior to this test, a new coal feed system was installed on the CFBC. Existing components incorporated into the feed system, which are also used for the EERC gasification system adjacent to the CFBC, include removable storage hoppers for transporting the coal (approximately 1500 kg of coal per hopper), a fixed coal feed bin, a drag chain apparatus for carrying the coal

from the bin up to the top, and a diverter valve. A new auger was installed to move the coal over from below the diverter valve. An existing EERC feeder was installed for measuring and controlling the coal feed rate to the CFBC. Other components installed included a coal feed rotary valve to help isolate the feed system from the operational combustion pressure and a pneumatic assist to carry the coal into the combustor. No significant problems were encountered with the new feed system.

The bed material composition was dominated by silica, which is to be expected when silica sand is used as start-up bed material. The high aluminum content (30%) of the coal ash also contributed to high aluminum levels in all three ash streams. Aluminum was twice as high in the baghouse than in either the bed or downcomer (26% to 29%, compared to 11% to 15%) but closely matched to high aluminum content in the coal (30%). Calcium in all three ash streams increased with the addition of limestone in Test 2 and increased again when the limestone feed rate was doubled in Test 3. Most of the calcium ended up in the baghouse ash. Possibly a slightly coarser grind on the limestone might keep more limestone in the bed longer for improved use of the limestone.

Relatively low carbon combustion efficiencies were obtained with this coal along with accompanying high carbon monoxide emissions. Higher operating temperatures might help improve combustion efficiency and decrease carbon monoxide emissions but could result in lower sulfur dioxide emissions. The projected boiler efficiency was reasonably good with this coal, even though there were higher-than-typical losses because of the large amount of unburned carbon; the low moisture content of this coal helped offset that factor. The heat-transfer coefficients measured with this coal are typical of what has been obtained with other fuels tested with the EERC CFBC pilot plant.

Uncontrolled SO_2 emissions, corrected to 6% oxygen, were about 580 ppm (about 1656 mg/Nm^3). The inherent sulfur retention was 37%. With the addition of limestone at a calcium/sulfur ratio of slightly greater than 1 in Test 2, SO_2 emissions were reduced to about 342 ppm, or 62% sulfur retention. Test 3 sulfur capture, with a limestone addition of approximately 2.4, was 82%, with a corrected emission level of 156 ppm. Even though there was very little calcium in the coal ash, the high ash content and low sulfur content meant that the inherent Ca/S ratio was about 0.7. The coal calcium appeared to have a high reactivity/availability, providing a better-than-expected level of sulfur capture without limestone addition.

NO_x emissions (corrected to 6% O_2) ranged from 542 to 613 ppm. This is significantly higher, more than double the NO_x emissions typically seen with the other coals tested at the EERC CFBC. The coal nitrogen on a heating value basis was about a factor of 1.5 times higher than other high-nitrogen-concentration coals previously tested at the EERC, but this in itself does not explain the higher-than-expected NO_x emissions. Other factors that would tend to increase NO_x emissions include operation at high velocity and operation at high excess air. It is possible that some adjustments to OFA could reduce these emissions, but the most likely course of action if NO_x emission reduction is required would be ammonia or urea injection.

This coal overall is a very good candidate for CFBC. The sulfur content is low, and good inherent sulfur capture results in relatively low sulfur dioxide emissions, even without limestone

addition. The limestone selected was also effective for the capture of sulfur with this coal. This coal has good handling properties and should not present any significant handling problems for a commercial feed system. There were no indications of any agglomeration or fouling potential with this coal.

Subtask 4.16 – Cancelled

Subtask 4.17 – Updating the "Improved Guidelines for Solving Ash Deposition Problems in Utility Boilers" Report

Program Area:	CRDP
Period of Performance:	8/15/10–2/28/11
Funding:	DOE: $32,102; Nonfederal: $59,633; Total: $91,735
EERC Subtask Manager:	Stelios Arvelakis
DOE Technical Monitor:	Vito Cedro
Nonfederal Partner:	EPRI
Final Report:	Arvelakis, S. *Subtask 4.17 – Updating the Improved Guidelines for Solving Ash Deposition Problems in Utility Boilers Report*; Final Report (Aug 15, 2010 – Feb 28, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-02-01; Energy & Environmental Research Center: Grand Forks, ND, Feb 2011.

In Subtask 4.17, the EERC participated in a project to update and improve EPRI's guidebook entitled *Improved Guidelines for Solving Ash Deposition Problems in Utility Boilers*. The document was reviewed and information updated and corrected as necessary, and new material was added to Chapters 9–12, 15–21, and 23. Comments from EPRI and DOE were also incorporated into the final version.

Subtask 4.18 – Testing of Indian Coal in a Transport Reactor Integrated Gasification (TRIG™) System

Program Area:	CRDP
Period of Performance:	1/15/11–5/31/11
Funding:	DOE: $110,448; Nonfederal: $204,999; Total: $315,447
EERC Subtask Manager:	Michael Swanson
DOE Technical Monitor:	Meghan Napoli
Nonfederal Partner:	Kellog, Brown and Root, Inc. (KBR)
Final Report:	Swanson, M.L. *Subtask 4.18 – Testing of Indian Coal in a Transport Reactor Integrated Gasification (TRIG™) System*; Final Report (Jan 15, 2011 – May 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-05-07; Energy & Environmental Research Center: Grand Forks, ND, July 2011.

Subtask 4.18 was undertaken to test Indian coal in the TRIG system. One of the more recent gasification technologies being commercialized is the TRIG technology offered by KBR. This technology is based on KBR's previous experience with fluid catalytic crackers in the petroleum industry. The TRIG functions as a circulating fluid-bed gasifier operating in the near-pneumatic transport regime of solid particle flow. This gasifier concept provides excellent gas–solid contacting of relatively small particles to promote high gasification rates and also provide the highest coal throughput per unit cross-sectional area of any gasifier, thereby reducing the capital cost of the gasification island.

The transport reactor has been extensively demonstrated as a viable air- or oxygen-blown gasification system at both the EERC and the Power Systems Development Facility in Wilsonville, Alabama. Previous testing and analysis of a transport reactor have indicated that the transport reactor performs better with higher-reactivity feedstocks (including subbituminous and lignitic coals and biomass mixtures) but has also successfully gasified high-volatile bituminous coals. High-ash feedstocks work best in moderate-temperature gasifiers like the TRIG system that do not require the ash to be slagged. For high-ash coals, the thermal penalty associated with the heat of melting for the ash can be very significant, so gasifiers that do not slag the ash are preferred.

The project approach was to conduct a single 200-hr oxygen-blown gasification test on two high-ash Indian coals in the existing pilot-scale transport reactor located at the EERC. Testing at the transport reactor development unit (TRDU) scale would be the lowest-cost option for determining the technological and economic hurdles that a transport reactor operating in an oxygen-blown mode on this high-ash fuel would face. Test parameters investigated included operating temperature, oxidant/carbon ratio, steam/carbon ratio, and coal type. Concerns for this feedstock included the potential for operational issues (e.g., bed agglomeration) associated with the higher gasification temperatures that may be necessary to improve carbon conversion and reduce the trace amount of higher hydrocarbons formed during the gasification process. 187 hr of fuel feed resulted in 168 hr of oxygen-blown gasification testing. Four fuel blends, representing low- and high-ash variants of the Mine A and Mine B coals, were processed. Carbon conversions ranging from 86 to 94 wt% were attained with the Indian coals, with the highest value achieved at gasifier temperatures between 920° and 980°C. Correction for the nitrogen flows and higher system heat loss produced fuel gas HHVs in the range of 220 to 230 Btu/dscf, which exceeds the 200-Btu/scf target metric. These HHVs are similar to oxygen-blown results on the TRDU with other coals.

During the first week of testing, operation of the hot-gas filter vessel and removal of collected ash were impaired by the breakage of three iron aluminide candles. Damage to the candles was determined to have resulted during the conclusion of a previous TRDU run and not from the testing of the Indian fuels. After replacement of the damaged candles, the hot-gas filter system presented no issues, even with the high ash loading to the filter system.

Two Indian coals from two mines in India were blended to produce blends representing nominally 40 wt%, or low-ash, and nominally 50 wt%, or high-ash, feed streams. A 2^3 factorial design test plan using operating temperature, oxidant/carbon ratio, and feedstock type as test parameters was formulated by the EERC and approved by KBR.

A 200-hr oxygen-blown gasification test was conducted during the first 2 weeks of March. Four fuel blends, representing low- and high-ash variants of the two coals were processed. Carbon conversions ranging from 86 to 94 wt% were attained with the Indian coals, with the highest value achieved at gasifier exit temperatures between 768° and 782°C. There appeared to be no issues with operation of the hot-gas filter system associated with the high ash loading resulting from processing of the Indian coals.

Subtask 4.19 – Pilot-Scale Mercury Testing for Advanced Fuel Research, Inc.

Program Area:	IEP
Period of Performance:	1/15/11–8/31/11
Funding:	DOE: $25,058; Nonfederal: $46,629; Total: $71,687
EERC Subtask Manager:	Ye Zhuang
DOE Technical Monitor:	Andrew Jones
Nonfederal Partner:	Advanced Fuel Research, Inc. (AFR)
Final Report:	Zhuang, Y. *Subtask 4.19 – Pilot-Scale Mercury Testing for Advanced Fuel Research, Inc.*; Final Report (Jan 15, 2011 – May 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-08-01; Energy & Environmental Research Center: Grand Forks, ND, July 2011.

In Subtask 4.19, a pilot-scale combustion test was performed to evaluate the mercury removal performance of AC sorbent PK1ACO1, a tire-derived sorbent provided by AFR for and on behalf of Canadian Carbon Converters, Inc. (CCC) in a low-sulfur coal flue gas. A Colombian coal was selected as the test coal. AC injection occurred upstream of an ESP that was maintained at a temperature of 149°C (300°F) during the test, and the injection rates ranged from 2.7 to 14.7 lb/Macf. For the purpose of comparison, DARCO® Hg, a commercial AC by Norit, was also tested for mercury removal under the same flue gas conditions.

One CMM was used at the ESP outlet to monitor gaseous mercury emissions for each test condition. Mercury ST samples, EPA M30B, were also collected for selected tests to verify CMM measurement. Under the test conditions in this study, PK1ACO1 attained mercury removals of 24.8%, 43.2%, 59.7%, and 65.4% at the injection rates of 2.7, 4.6, 9.2, and 14.7 lb/Macf, respectively. The performance of the PK1ACO1 on mercury capture was found to be slightly better than that of DARCO Hg carbon under the similar testing conditions.

Subtask 4.20 – Testing of High-Ash Chinese Coal in a Transport Reactor Integrated Gasification (TRIG) System

Program Area:	CRDP
Period of Performance:	12/15/10–9/30/11
Funding:	DOE: $110,448; Nonfederal: $204,999; Total: $315,447
EERC Subtask Manager:	Michael Swanson
DOE Technical Monitor:	Meghan Napoli
Nonfederal Partner:	KBR
Final Report:	Swanson, M.L.; Henderson, A.K.; Laudal, D.A. *Subtask 4.20 – Testing of High-Ash Chinese Coal in a Transport Reactor Integrated Gasification (TRIG™) System*; Final Report (Dec 15, 2010 – Sept 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-09-02; Energy & Environmental Research Center: Grand Forks, ND, Sept 2011.

In Subtask 4.20, a high-ash Chinese coal was tested in the TRIG system. DOE NETL's Office of Coal and Environmental Systems has as its mission developing advanced gasification-based technologies for affordable, efficient, zero-emission power generation. These advanced power systems, which are expected to produce near-zero pollutants, are an integral part of DOE's Vision 21 Program. DOE has also been developing advanced gasification systems that lower the capital and operating costs of producing syngas for chemicals production.

One of the more recent fluidized-bed gasification concepts to be investigated is that of the transport reactor gasifier, which functions as a circulating fluid-bed gasifier while operating in the near-pneumatic transport regime of solid particle flow. This gasifier concept provides excellent gas–solid contacting of relatively small particles to promote high gasification rates and provides the highest coal throughput per unit cross-sectional area of any gasifier, thereby reducing the capital cost of the gasification island. The transport reactor has been extensively demonstrated as a viable air- or oxygen-blown gasification system.

Over 3900 hr of operation on more than a dozen different coals ranging from bituminous to lignite, along with a petroleum coke, had been completed at the time of this project in the pilot-scale TRDU at the EERC. The EERC established an extensive database on the operation of these various fuels in both air- and oxygen-blown modes using a pilot-scale transport reactor gasifier. This database has been useful in determining the effectiveness of design changes on an advanced transport reactor gasifier and for determining the performance of various feedstocks in a transport reactor.

The effects of different fuel types on both gasifier performance and the operation of the hot-gas filter system have been determined. Carbon conversions up to 89% have also been obtained and are dependent on the gasifier temperature and oxygen/coal ratio. Higher-reactivity (low-rank) coals appear to perform better in a transport reactor than the less reactive bituminous coals. Factors that affect TRDU product gas quality are coal type, temperature, and air/coal ratios.

Testing with two high-ash bituminous coals from China was completed in Subtask 4.20, with 4 plus days of continuous testing. The highest carbon conversion numbers were attained at an average mixing zone gasification temperature around 980°C with a gasifier exit temperature around 770°C. No issues with agglomeration were observed with either feedstock.

Subtask 4.21 – Evaluation of a Spray Dryer Absorber for Multipollutant Control

Program Area:	CRDP
Period of Performance:	12/15/10–5/31/12
Funding:	DOE: $368,356; Nonfederal: $516,200; Total: $884,556
EERC Subtask Manager:	Denny Laudal
DOE Technical Monitor:	Andrew Jones
Nonfederal Partner:	FMC Corporation
Final Report:	Laudal, D.L.; Thompson, J.S. *Subtask 4.21 – Evaluation of a Spray Dryer for Multipollutant Control*; Final Report (March 1, 2011 – May 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-05-05; Energy & Environmental Research Center: Grand Forks, ND, May 2012.

In Subtask 4.21, a spray dryer technology was evaluated for multipollutant control. In 2011, the Cross-State Air Pollution Rule (and previously, the Clean Air Interstate Rule) was promulgated. As a result, there was significant interest in technologies to reduce NO_x emissions by the utility and small boiler industries. FMC Corporation has a technology using H_2O_2 injection to oxidize NO to NO_2 or higher oxidized forms of nitrogen that would be more readily removed using currently installed wet and dry FGD systems. Although previous testing demonstrated the potential of this approach, much was unknown regarding the level of NO_x control that could be achieved for a SDA FGD system. The primary objective of Subtask 4.21 was to understand and improve NO_2 capture as well as identify potential cobenefits of improved mercury capture.

Over the course of the project, five test plans were developed and completed on the EERC pilot-scale combustor. Each of the test plans included a set of variables and a sequence of tests to be run to generate the required data. Four different fuels—natural gas, a PRB coal (Absaloka), a low-sulfur bituminous coal from West Virginia, and North Dakota lignite from Coal Creek (Falkirk) power plant—were tested. The major focus for each test plan was as follows:

- Test Plan 1 – A number of operation variables were tested while natural gas was fired to determine their effect on NO_2 and SO_2 removal across the SDA and fabric filter.

- Test Plan 2 – The second test plan was essentially the same as the first except a PRB coal was fired in the combustor rather than natural gas.

- Test Plan 3 – The PRB coal was fired as a series of additives or combinations of additives were tested in an attempt to improve the NO_2 and SO_2 removal across the SDA.

- Test Plan 4 – These tests focused on NO oxidation via H_2O_2 injection at the same time as a series of operational variables were tested.

- Test Plan 5 – Based on the previous results, it was determined that residence time at temperature for H_2O_2 injection was a critical variable. Therefore, a residence time chamber was designed, built, and put in place, followed by a series of tests evaluating NO oxidation via H_2O_2 injection.

The results showed there was a small increase in NO_x and NO_2 removal across the SDA, with an increase in the Ca/S stoichiometric ratio. However, it appears to flatten out at about 2.5. There was a substantial increase in NO oxidation, with an increase in the molar ratio of H_2O_2 /NO. A critical variable was the H_2O_2 injection temperature. For the PRB coal, the NO_x removal was only at 10% at 600°F and about the same at 800°F (2-s residence time at temperature). However, when the temperature of injection was increased to 1000°F, the removal increased to 30% for the PRB and 55% for the West Virginia bituminous coal.

Of all the additives tested, none showed significant improvement in NO_x reduction across the SDA. However, several showed some beneficial effects depending on the fuel and other variables.

In addition to NO oxidation, there was also the potential that the injection of H_2O_2 could oxidize Hg^0 to Hg^{2+}, which would be beneficial because Hg^{2+} is soluble and could result in increased mercury control across the SDA. There appeared to be an increase in mercury removal across the SDA/fabric filter when H_2O_2 injection was used. However, it was dependent on a number of factors.

A concern was that the oxidation potential of the H_2O_2 could also increase the concentration of the SO_3 in the flue gas. The data indicate that when natural gas is fired and SO_2 externally added, a substantial conversion of SO_2 to SO_3 occurred. However, when coal is fired, this is somewhat mitigated. In all cases, the SO_3 was captured in the SDA/fabric filter.

Based on the results, the following conclusions were drawn:

- Removal of SO_2 and NO_x increased with increasing Ca/S stoichiometric ratio up to a maximum at a ratio of approximately 2.5.

- NO_x removal increased with higher SO_2 concentrations.

- Higher NO_2 concentrations (partitioning) resulted in higher removal.

- Some additives improved removal, albeit slightly.

- H_2O_2 injection directly correlates with NO oxidation for all fuels. Increased molar ratio of H_2O_2/NO resulted in improved NO oxidation and subsequent capture.

- Injection temperature and time at temperature are critical for increased NO oxidation. Increased injection temperature improved NO oxidation and subsequent capture.

- Sampling methodology to minimize transport and time is critical for NO/NO_2 (NO_x speciation) measurements.

- SO_2 concentration did not appear to affect NO oxidation with H_2O_2.

- The addition of H_2O_2 to the flue gas appeared to increase mercury oxidation.

- SO_3 generation from oxidation of SO_2 was apparent but minimal in most cases.

Subtask 4.22 – Extended Pilot-Scale Testing of the Pratt & Whitney Rocketdyne Compact Reformer

Program Area:	CRDP
Period of Performance:	3/15/11–11/14/12
Funding:	DOE: $364,426; Nonfederal: $514,635; Total: $879,061
EERC Subtask Manager:	Jay Almlie
DOE Technical Monitor:	David Lyons
Nonfederal Partner:	Pratt & Whitney Rocketdyne (PWR)
Final Report:	Almlie, J.C. *Subtask 4.22 – Extended Pilot-Scale Testing of the Pratt & Whitney Rocketdyne Compact Reformer*; Final Report (March 15, 2011 – Feb 28, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-11-03; Energy & Environmental Research Center: Grand Forks, ND, Nov 2012.

In Subtask 4.22, extended pilot-scale testing of PWR's compact reformer was performed. Hydrogen is a key chemical building block in many industrial processes. In fact, a vast majority of hydrogen produced today is used for petrochemical processes, many of which directly involve the fossil energy sector. PWR is developing a hydrogen generator using a technology that is an alternative to traditional steam methane reforming (SMR). This hydrogen generator represents a step change in production efficiency and capital costs associated with hydrogen production. PWR's alternative technology employs a proprietary regenerative sorbent process and is capable of producing large quantities of high-purity hydrogen with many forecasted advantages over SMR technology.

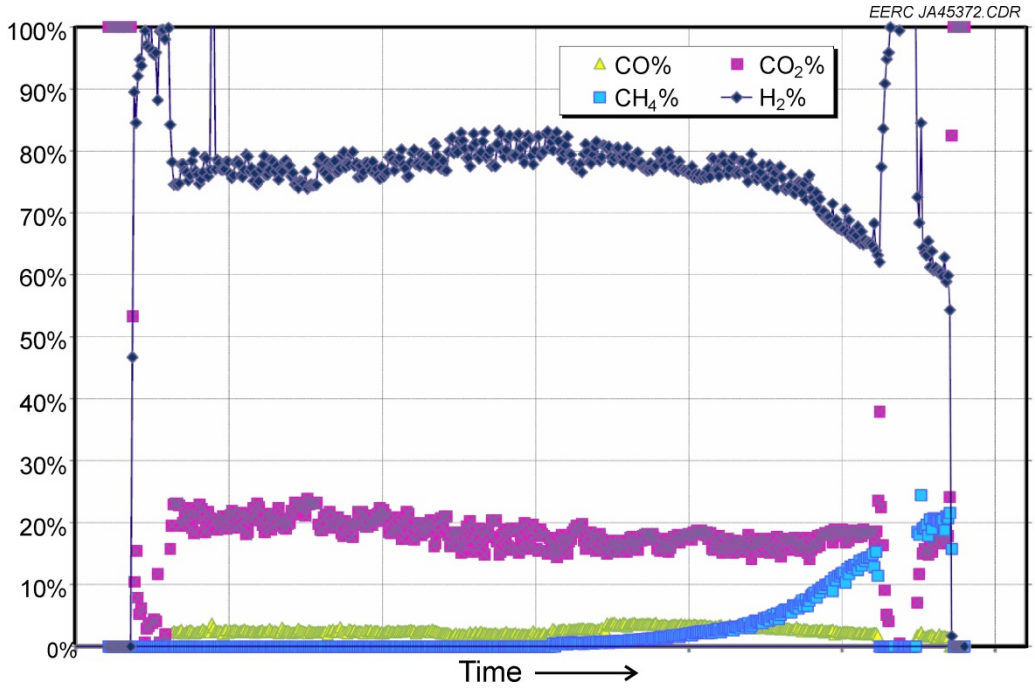
During the course of this project, PWR and the EERC pursued catalyst studies and other tests at bench scale to investigate the root causes of catalyst deactivation in past subscale unit tests. The EERC bench tests were designed to systematically eliminate branches from the fault tree developed by the project team. This approach eventually focused the team on certain compounds found in the burner refractory material. However, it was not clear whether the catalyst substrate was taking part in the catalyst blinding/blocking reactions or the blinding/blocking phenomenon was entirely because of the burner refractory compounds (contaminants). Tests that most closely

resembled the failure modes of previous subscale tests produced a similar failure (increased methane slip with no improvement after the hydrogen reduction step). With this information in hand, the project team proceeded to subscale tests to validate these answers and to prove methods of avoidance of these failure conditions.

Results obtained from bench-scale tests guided the project team to complete several hardware changes to the feasibility demonstration unit (FDU) test hardware in an effort to preclude further blinding reactions on the catalyst. First, a superalloy metal liner was inserted into the main burner to preclude abrasion of the refractory liner of the burner. Because bench-scale tests also indicated a strong sensitivity of the blinding reaction to temperature, tighter control over temperature in the calciner and hydrogen reactor vessels was also obtained with higher-wattage electrical heaters and additional insulation. Finally, several software controls were integrated to help the test operations team maintain tighter thermal and flow control.

Prior to FDU test operations in March 2012, a great deal of planning effort was committed to ensure the greatest possible success. Operating manuals were thoroughly refined to incorporate most recent lessons learned, the operations team was thoroughly briefed on pitfalls to avoid during test operations, and a clear decision tree for test operations was defined to guide the test team.

Despite execution of these design changes and operational changes, FDU tests showed that the catalyst again deactivated in a manner similar to the manner observed in December 2010. Hydrogen product gas measurements are shown in the figure below.



Hydrogen production results from March 2012 FDU test.

These curves closely resemble the earlier results obtained in 2010. The data show a distinct falloff in hydrogen production and a coupled increase in methane slip after only a few hours of

operation. This data set now points to an alternate mechanism that is causing a semipermeable crust to form on the catalyst during the course of hydrogen production, thus decreasing hydrogen production with process operation time.

Subsequent tests were intended to investigate the use of alternative catalyst substrates, if required, to avoid the blocking/blinding phenomena. However, after the March 2012 test, PWR decided to discontinue the project until further research internal to PWR could present a solution with a strong probability of success. At the close of this subtask, PWR continued to believe that solutions could be found to the risks identified by this technology development effort and intended to resume activity in 2013 after evaluating the most cost-effective approach to arriving at a solution.

Subtask 4.23 – Pilot-Scale Testing Evaluating the Effects of Bromine Addition on CMMs at Low Mercury Concentrations

Program Area:	IEP
Period of Performance:	6/1/11–5/31/12
Funding:	DOE: $126,156; Nonfederal: $227,972; Total: $354,128
EERC Subtask Manager:	Denny Laudal
DOE Technical Monitor:	Andrew Jones
Nonfederal Partners:	CATM Affiliates Program, EPRI, and University of Wyoming School of Energy Resources
Final Report:	Laudal, D.L.; Thompson, J.S. *Subtask 4.23 – Pilot-Scale Testing Evaluating the Effects of Bromine Addition on CMMs at Low Mercury Concentrations*; Final Report (June 1, 2011 – May 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-05-10; Energy & Environmental Research Center: Grand Forks, ND, May 2012.

In Subtask 4.23, pilot-scale testing was performed to evaluate the effects of bromine addition on CMMs at low Hg concentrations. EPA finalized NESHAPs for the utility industry in December 2011. The floor for Hg emissions was determined using the MACT basis under Section 112 of the 1990 CAA Amendments. As a result, many plants in the eastern and western United States will be required to control and continuously measure Hg concentrations at less than 1.0 µg/m^3 of gas. It is expected that many of the plants burning Wyoming PRB coal will be required to use either brominated compounds or BACs to comply with the MACT standard. There appears to be some evidence that bromine in the flue gas can result in interferences, biasing CMM results (1, 2). As a result, Subtask 4.23 was undertaken to evaluate the two CMMs most widely used by the utility industry: the Tekran Model 3300 and the Thermo Scientific Mercury Freedom system.

The primary goal of the project was to determine the effects of bromine on the accuracy and precision of CMMs at Hg concentrations <1.0 µg/Nm^3. Specific objectives were as follows:

- Verify the accuracy of carbon trap measurements via quad train sampling and spiked traps while sampling bromine-laden flue gas for Hg.

- Determine the accuracy and variability of the CMM measurements while natural gas is burned, with Hg and bromine added under controlled conditions.

- Determine the accuracy and variability of the CMM measurements while Wyoming PRB coal is burned, with Hg control to levels <1.0 µg/m^3.

To accomplish these objectives, pilot-scale tests were conducted, and the accuracy of the instruments was determined by comparison to the reference method, EPA M30B (STs). The project also required that the variability of the ST sampling be determined. Therefore, to assess the precision of the STs, quad train samples were taken. In addition, spiked and blank samples were analyzed. All of this required a very high level of QA/QC to ensure that all equipment (pilot-scale combustor, Hg-spiking systems, HBr injection system, ST-sampling equipment, Ohio Lumex ST analyzer, and CMMs) was calibrated properly and operating optimally during the testing phase.

The overall approach to determining the effect of bromine on CMMs at Hg concentrations <1.0 µg/Nm^3 was to compare the CMM results to those obtained based on a reference method (EPA M30B). To do this, three primary activities were completed. The first was the initial preparation of the equipment, and the other two were pilot-scale tests. Activity 1 was designed to ensure that all equipment (spiking systems, combustor, ST-sampling systems, Ohio Lumex ST analyzer, and CMMs) was operating at the highest level. The second was to complete 1 week of pilot-scale testing firing natural gas and adding Hg and bromine using the spiking systems developed at the EERC. The third was to complete 1 week of testing firing a Wyoming PRB coal in the EERC pilot-scale combustor while using HBr and/or BACs to reduce the Hg concentration to <1.0 µg/Nm^3. The test plans are shown in the table below and the table on the top of page 153.

Test Plan Firing Natural Gas

Test Condition	Spiked Hg Location	AC	HBr Injection, ppmv	Nominal Hg Conc., µg/Nm^3
NG1	Baghouse outlet	None	5	0.25
NG2	Baghouse outlet	None	5	0.75
NG3	Baghouse outlet	None	25	0.25
NG4	Baghouse outlet	None	25	0.75
NG5	Combustor	Hg-LH[1]	None	0.25
NG6	Combustor	Hg-LH	None	0.75
NG7	Combustor	Hg[2]	5	0.75
NG8	Combustor	Hg	5	0.25
NG9	Combustor	Hg	25	0.25
NG10	Combustor	Hg	25	0.75

[1] Norit America DARCO® Hg-LH (BAC).
[2] Norit America DARCO Hg (AC).

Test Plan Firing Wyoming PRB Coal

Test Condition	AC	HBr Injection, ppmv	Nominal Hg Conc., µg/Nm^3
C1	Hg	None	0.75
C2	Hg	None	0.25
C3	Hg-LH	None	0.75
C4	Hg-LH	None	0.25
C5	Hg	5	0.75
C6	Hg	5	0.75
C7	Hg	25	0.25
C8	Hg	25	0.75

The approach for the pilot-scale test was to compare the results obtained using the Tekran and Thermo Scientific CMMs to those using the ST reference methodology (EPA M30B). The STs are shown in the tables below. The actual Hg concentrations are based on the ST results. ST analysis was completed by the EERC using the Ohio Lumex ST analyzer.

STs Test-Firing Natural Gas

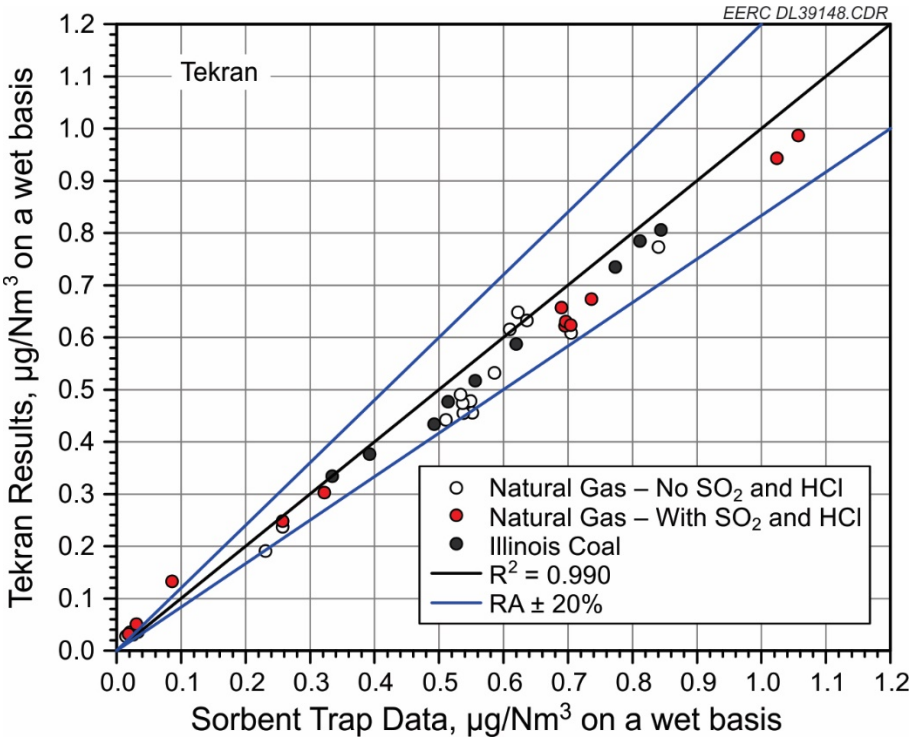
Test Condition	No. Standard Traps	No. Speciation Traps	Sample Time, hr	Nominal Hg Conc., µg/Nm^3	Actual Hg Conc., µg/Nm^3
NG1	2		3	0.25	0.258
NG2	2		3	0.75	0.707
NG3	2		3	0.25	0.168
NG4	2		3	0.75	0.602
NG5	2		3	0.25	0.047
NG6	2		3	0.75	0.565
NG7	2		3	0.75	1.13
NG8	2		3	0.25	0.159
NG9	2	2	3/2*	0.25	0.266
NG10	4	2	3/2*	0.75	0.757

*3/2 represents 3 hr for the standard trap and 2 hr for the speciation trap.

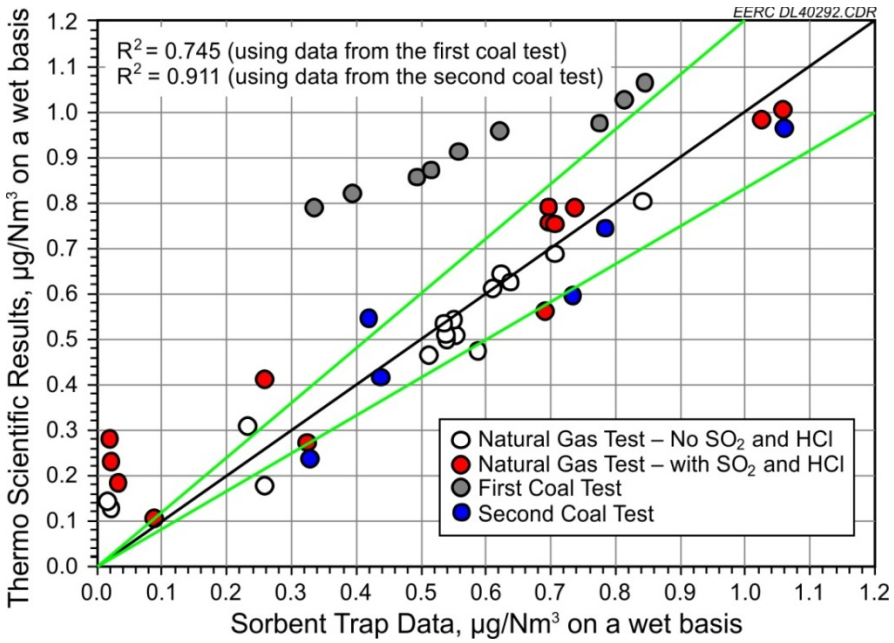
STs Test-Firing Wyoming PRB Coal

Test Condition	No. Standard Traps	No. Speciation Traps	Sample Time, hr	Nominal Hg Conc., µg/Nm^3	Actual Hg Conc., µg/Nm^3
C1	4		3	0.75	0.929
C2	4		3	0.25	0.573
C3	4		3	0.75	0.773
C4	4		3	0.25	0.364
C5	4		3	0.75	0.638
C6	4		3	0.25	0.371
C7	4		3	0.75	1.26
C8	4	2	3/2*	0.25	0.768

Previous testing showed that, without the use of HBr and/or BAC injection, both instruments performed very well for a range of sulfur dioxide, hydrogen chloride, and oxygen gas conditions when either natural gas or coal was fired (3). The Tekran instrument provided a lower quantitation limit compared to the Thermo Scientific instrument: 0.01 µg/Nm^3 compared to 0.04 µg/Nm^3. The results are summarized in the figure below and the figure on the top of page 155. Testing under this subtask showed an impact of bromine addition on the Tekran CMM while natural gas was fired, resulting in a calculated relative accuracy (RA) of 57% compared to the ST method. The firing of Wyoming PRB coal limited the effects, resulting in a RA of 19%.

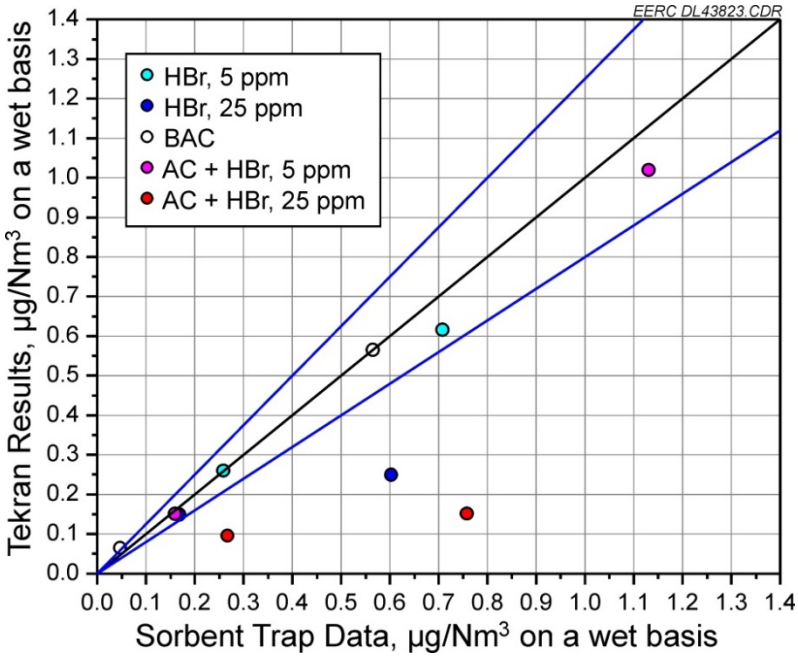


Summary of baseline Tekran CMM.

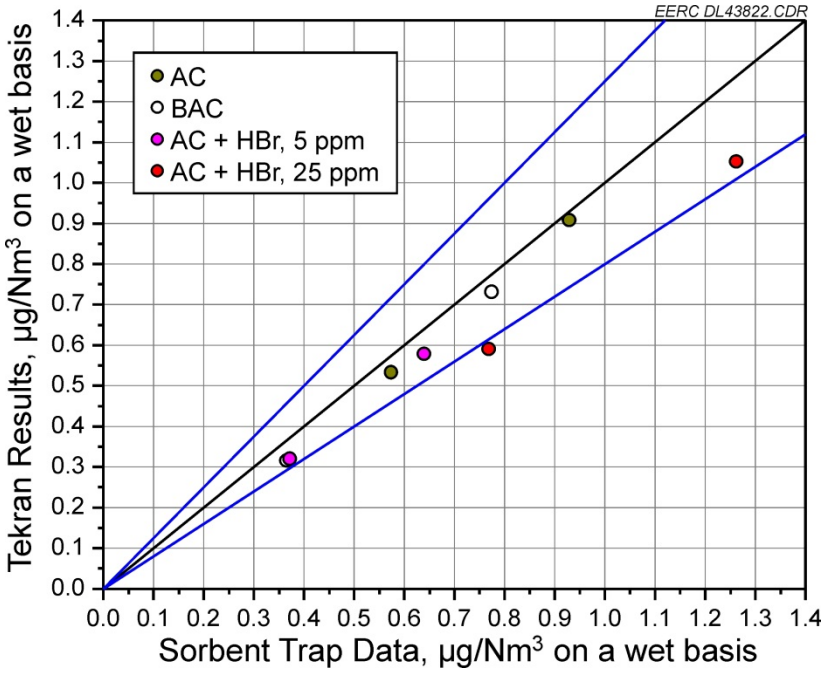


Summary of baseline Thermo Scientific CMM results.

The results for the Tekran data are summarized in the figure below and the figure on the top of page 156.

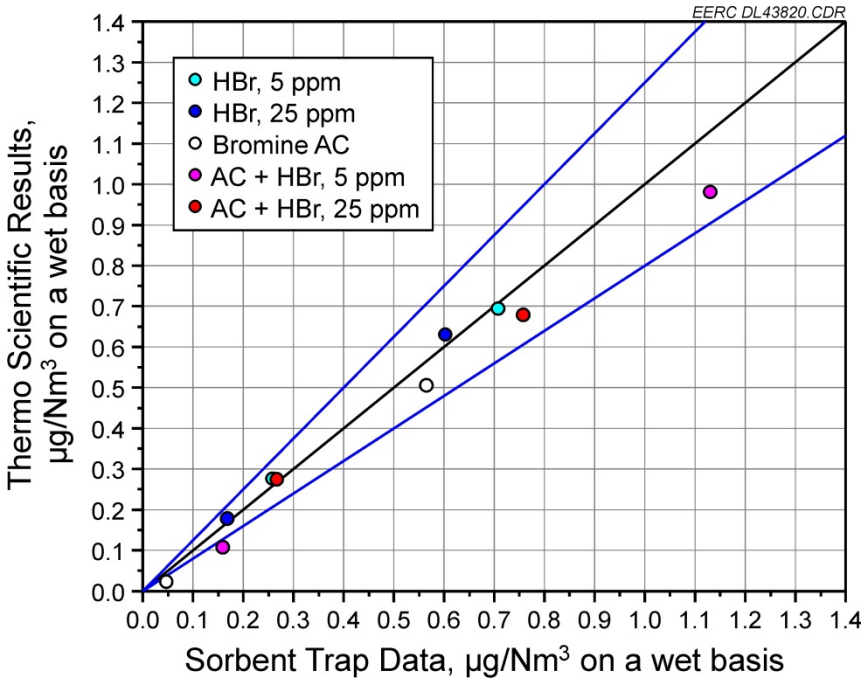


Summary of Tekran CMM results when natural gas with bromine addition was fired.

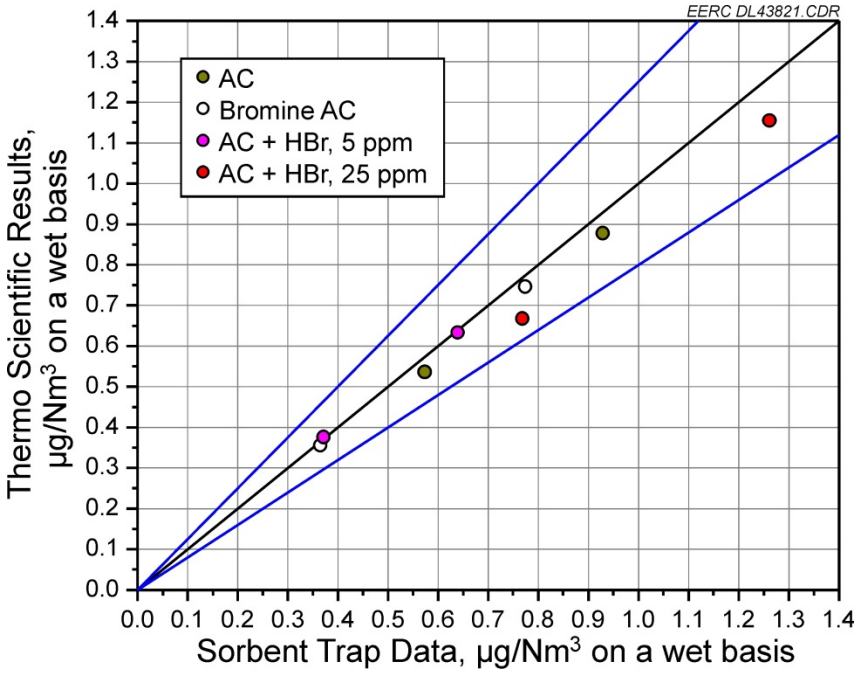


Summary of Tekran CMM results when Wyoming PRB coal with bromine addition was fired.

The results obtained with the Thermo Scientific instrument, shown in the figure below and the figure on the top of page 157, were similar to the previous testing without bromine addition, giving an overall RA of 10%.



Summary of Thermo Scientific CMM when natural gas with bromine addition was fired.



Summary of Thermo Scientific CMM results when Wyoming PRB coal with bromine addition was fired.

It should be noted that the greatest deviation was for bromine injection levels of >10 ppmv. This is a substantially higher concentration than what would be injected in a full-scale application.

Based on the results from these tests, the following conclusions and observations can be made:

- Overall, the CMMs operated very reliably, with very few problems encountered. The CMMs were operated continuously over the 3 weeks, including the time when the PTC was not being operated (CMMs sampled ambient air), with very little input from EERC personnel.

- The EERC mercury-spiking systems worked well and were consistent.

- Compared to the ST data, the Thermo Scientific CMM worked well when both natural gas and PRB coal were fired, with and without the addition of HBr. The Thermo Scientific CMM RA for the natural gas test was 14.6%, for the Wyoming PRB coal test was 10.4%, and for all 18 tests was 10.2%.

- The Tekran CMM showed a bias low when HBr was added to the flue gas as part of the test matrix. The bias was less severe when coal was fired. Compared to the ST data, the Tekran CMM RA for the natural gas test was 57.8%, 19.1%, for the coal test, and averaged 32.2% for all 18 tests. The difference between the STs and the Tekran CMM appears to be systemic in nature, as the CMM results were consistently lower than those measured using the STs when HBr was present.

References
1. Pavlish, J.H.; Thompson, J.S.; Martin, C.L.; Musich, M.A.; Hamre, L.L. *Field Testing of Activated Carbon Injection Options for Mercury Control at TXU's Big Brown Station*; Final Report (March 2, 2005 – March 31, 2008) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-05NT42305 and Luminant Power; EERC Publication 2008-EERC-01-05; Energy & Environmental Research Center: Grand Forks, ND, Feb 2008.
2. CATM Staff. *2008 Annual Report for the Center for Air Toxic Metals*. Energy & Environmental Research Center: Grand Forks, ND; www.undeerc.org/catm/pdf/area2/2008SamplingandAnalyticalMethods.pdf (accessed May 2008).
3. Laudal, D.L.; Thompson. J.S.; Subtask 4.10 – *Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations*; Final Report (March 1, 2010 –June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; Energy & Environmental Research Center: Grand Forks, ND, 2011.

Subtask 4.24 – Field Evaluation of Novel Approach for Obtaining Metal Emission Data

Program Area:	IEP
Period of Performance:	7/15/11–12/31/13
Funding:	DOE: $364,805; Nonfederal: $557,020; Total: $921,825
EERC Subtask Manager:	John Pavlish
DOE Technical Monitor:	Barbara Carney
Nonfederal Partners:	CATM Affiliates Program, EPRI, Great River Energy (GRE), Minnesota Power, Montana–Dakota Utilities Co., NDIC, Ohio Lumex, and SaskPower
Final Report:	Pavlish, J.H.; Laudal, D.L.; Thompson, J.S. *Subtask 4.24 – Field Evaluation of Novel Approach for Obtaining Metal Emission Data*; Final Report (July 15, 2011 – Dec 31, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-12-09; Energy & Environmental Research Center: Grand Forks, ND, Dec 2013.

In Subtask 4.24, SF10, and numerous proprietary sorbents provided by Grünergy Technologies. SF10 was injected the applicability and performance of the MEST method was evaluated for metals (MEST-M) and for HCl (MEST-H) to accurately measure stack emissions at three North Dakota lignite-fired power plants. Over the past two decades, emissions of mercury, nonmercury metals, and acid gases from energy generation have become the focus of regulatory rule making. On February 16, 2012, EPA promulgated the Mercury and Air Toxics Standards (MATS) to reduce mercury, nonmercury metals, and HCl emissions from coal-fired power plants (1). The reference method for halogens is EPA M26 or M26A. EPA M26 (nonisokinetic) and EPA M26A (isokinetic) are wet-chemistry, impinger-based methods that are designed to collect both acid gas and halogen gas species present in flue gas. M26A must be used if entrained water droplets are present in the flue gas. The reference method for mercury and nonmercury metal HAPs is EPA M29. There are a number of concerns regarding the use of EPA M26/26A and M29 to meet the MATS requirements, including the following:

- The methods are difficult to use, require highly trained personnel, and involve substantial preparation.

- The methods use toxic chemicals that are a concern for safety, handling, shipping, and ultimate disposal.

- A very high level of QC is required, not only for sample analysis but for sample-collecting activities.

- The detection limits for M29 may not be adequate in some cases to measure accurately at the existing unit limits established under MATS. Several of the new/reconstructed unit limits (e.g., As, Be, Co, and Cd for coal and new continental liquid oil units) are well below the capabilities of the method.

- Inclusion of mercury in a M29 test creates a risk of contaminating the sample with manganese, because of the additional permanganate impinger that must be added to the sampling train.

As a potential alternative to EPA M29 and M26/26A, the EERC developed a MEST method with two separate sampling applications: one for metals (MEST-M) and one for halogens (MEST-H). The overall goal of this project was to evaluate the applicability and performance of the MEST method for measuring trace metal and HCl emissions at three North Dakota lignite-fired power plants.

A comparative study of the MEST-H method and EPA M26A was performed for the three test sites. At Plants 1 and 2, the HCl results showed no significant bias for the MEST-H method compared to M26A, and the precision of both methods was very good. At Plant 3, a significant bias was observed between the two methods for HCl; EPA M26A measurements were below detection limits, while the ME-ST-H measurements were higher. This was most likely a result of water droplet formation in the wet stack. Wet stacks have been shown to be problematic for EPA M26A (2).

Although all three sites used North Dakota lignites, there were substantial differences in the metal emissions among the three sites. At Plant 1, Sb, As, Be, Cd, and Co emissions were below the detection limits for both methods. Hg was well above detection limits. For EPA M29 samples, there were significant background levels in the method blanks for Cr, Pb, Mn, and Ni. For the MEST-M method, high blank values were a problem for Cd, Cr, Pb, Mn, and Ni. As a result, blanks were elevated for nine of the 11 metals (Hg and Se were the exception), and modifications were made to the sorbent material for the MEST-M method to reduce the background blanks for the various trace metals.

At Plant 2, Sb, Be, and Cd were below the detection limits for EPA M29, but all trace metals of interest were above the detection limits for the ME-ST-M method. Although the sorbent material was modified, background levels were measurable, i.e., above detection limits, for eight of the 11 metals. For Cr, Mn, and Ni, the background levels were such that the QA/QC limit (blank $\leq$30% of the sample value) was not met.

At Plant 3, all metals except Sb were above the detection limits for EPA M29. However, for Cr, Mn, and Ni, the EPA M29 blanks were >30% of the measured value, resulting in an invalid sample. Although the measured values were all above the detection limits of the MEST-M method, after each of the trace metals was corrected for the blank, Cd, Cr, Pb, and Ni were below the detection limits. The only trace metal having a blank value >30% for the MEST-M method was Mn.

Although the three data sets obtained in this project are too few for a complete EPA M301 validation study, this procedure was used to statistically compare the MEST-M and MEST-H methods to the EPA reference methods, M29 and M26A, respectively. According to M301, a valid statistical comparison between the two trace metal-sampling methods for individual trace metals can only be made if both methods have results above the detection limit and the background (blank) concentrations are ≤30% of the measured value. The overall results showed that the MEST-M concentrations measured for Hg, Se, Sb, As, Cd, and Co that were above the MATS limit showed good agreement between EPA M29 and the MEST-M method, generally within 20%.

Based on the results of these three field tests, the MEST-H method appears to be a good candidate as an alternative method to M26/26A. For the MEST-M method, additional research is needed to explore possible longer sampling durations and/or selection of lower-background materials containing near-zero Pb, Ni, Cr, and Mn before the MEST-M method can be considered as a potential alternative to M29.

References

1. National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units: Final Rule (Mercury and Air Toxics Standards [MATS]). 40 Code of Federal Regulations, Parts 60 and 63; *Fed. Regist*. **2012**, *77* (32), 9304.
2. Johnson, L.D. Stack Sampling Methods for Halogens and Halogen Acids. Presented at EPA–A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.

Subtask 4.25 – Cancelled

Subtask 4.26 – Demonstration of Multipollutant Reduction Using a Lextran 3-in-1 Wet Scrubber

Program Area:	CRDP
Period of Performance:	10/16/12–3/31/13
Funding:	DOE: $64,650; Nonfederal: $130,887; Total: $195,537
EERC Subtask Manager:	Jay Almlie
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	GRE, Lextran Ltd., and NDIC
Final Report:	Almlie, J.C. *Subtask 4.26 – Demonstration of Multipollutant Reduction Using a Lextran 3-in-1 Web Scrubber*; Final Report (Oct 16, 2012 – March 31, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-03-04; Energy & Environmental Research Center: Grand Forks, ND, March 2013.

In Subtask 4.26, a Lextran technology was evaluated at pilot scale. Extensive research has been performed over the years, and several technologies have been developed specifically for NO_x and SO_2, individually. Wet and dry lime-based scrubber technologies have been employed extensively to capture SO_2 emissions in commercial operations. Among existing commercially available de-NO_x technologies, only combustion-based de-NO_x technologies have proven successful in North Dakota utility plants. However, combustion modifications typically provide less than 50% NO_x reduction with undesired high levels of unburned carbon and CO. Alternatively, SCR that can provide up to 90% NO_x emission reductions in many coal-fired boiler applications is not applicable to Fort Union lignite-fired utility plants, primarily because of the high levels of alkali and alkaline-earth metals in the Fort Union lignites that fuel many North Dakota utility boilers.

Lextran has developed a unique multipollutant gas-cleaning technology that uses a Lextran liquid catalyst to simultaneously capture NO_x and SO_2 within a conventional wet scrubber. With the addition of ammonia, KOH, or other basic reagents, the captured SO_2 and NO_x is reformed into beneficial fertilizer by-products such as ammonium nitrate and ammonium sulfate or potassium sulfate and potassium nitrate. Oxidation of nitrous oxide to nitrogen dioxide is promoted by injection of ozone upstream of the wet scrubber.

The focus of Subtask 4.26 was on pilot-scale combustion tests to evaluate the effectiveness of this multipollutant gas-cleaning technology in typical North Dakota lignite flue gas conditions. The following summarizes the results of this testing, completed at the EERC in January 2013, to provide a preliminary evaluation to interested parties in North Dakota and at DOE.

The pilot-scale PTC at the EERC was employed to accomplish the tests. A wet scrubber attached to the system was modified to support the Lextran technology. Operational issues—including issues with pH probe compatibility with the Lextran emulsion, issues with emulsion mixing, and possible issues with ozone interference with continuous emission monitors (CEMs) employed in the test—prevented the team from accomplishing all of the test points delineated in

the text matrix defined prior to test execution. However, several key test points were accomplished that illustrate both the significant promise and the current development status of the Lextran technology relative to lignite-based flue gas applications.

During one of the key test points, the technology achieved an approximately 80% reduction in NO_x emissions at an ozone injection rate of 270 g/hr. The results of ozone injection are highly sensitive to flue gas temperature at the point of injection. When the ozone injection port was switched from upstream of the ESP to just upstream of the wet scrubber, NO_x reduction jumped from approximately 60% to greater than 85%. This provides a positive indicator of performance at a worst-case residence time. It is possible that the 85%+ NO_x reduction was limited only by the ozone generation capacity of the specific ozone injection hardware employed during this test.

Some of the same negative trending apparent in the NO_x data is also apparent in the SO_2 data. It results in an approximately 80% SO_2 capture efficiency. It is, however, important to note that SO_2 capture attained nearly 100% before ozone injection was started. This is further evidence of an unresolved question centered on the effect of large quantities of ozone on flue gas chemistry, ozone effects on SO_2 measurement, or some other unknown factor. During the same period, SO_3 was measured at the scrubber outlet to be approximately 41 ppmv.

At the end of the week of testing, the wet scrubber was configured to operate as a standard lime slurry scrubber. A lime slurry with 10 wt% calcium hydroxide solids was used for SO_2 control. As was expected, the wet scrubber accomplished complete SO_2 capture and no significant NO_x capture.

A brief summary of NO_x and SO_2 capture results is presented in the table below.

Summary of NO_x and SO_2 Capture

Test	NO_x In, ppmv	NO_x Out, ppmv	SO_2 In, ppmv	SO_2 Out, ppmv	NO_x Control, %	SO_2 Control, %
I-1*	547	86	938	231	84.3†	75.4*
II-3 (pre-O_3 injection)	–	–	1033	1	–	99.9
II-3 (modified)	498	175	1034	177	65–80†‡	82.9*
III-2	494	544	1046	0	−10.1	100.0
III-1	450	454	1047	0	−1.0	100.0

* Results in question due to uncertainty surrounding quality of emulsion mixing and ozone interference.
† May have been limited to only 85% by ozone generator limits.
‡ Higher NO_x control was achieved with shorter residence time indicating room for ozone optimization.

There is debate about the accuracy of the SO_2 out values during the Lextran tests (I-1 and II-3) and, therefore, the associated SO_2 control efficiency values. Additional investigations focused specifically on exclusion of ozone biases would be required to refine these numbers. Additionally, NO_x control efficiencies may have been limited by the ozone generation capability of the ozone generation hardware employed. Hence, these values should be interpreted only as indicators of unoptimized Lextran performance. Wet-chemistry sampling was also completed, the results of

which are summarized in the table below. The wet-chemistry sampling revealed that SO_3 emissions may warrant further investigation.

Summary of Wet-Chemistry Results

Test	SO_3 at WS Out, ppmv	HCl at WS Out, ppmv	$Hg_{(T)}$ at WS In, µg/m³	$Hg_{(T)}$ at WS Out, µg/m³	$Hg_{(T)}$ Capture, %
II-3	41.4	1.1	12.4	10.3	17.1
III-2	0.1	1.1	13.0	11.0	15.9

This testing represented the largest scale at which Lextran has tested this technology. The fact that it performed as well as it did during this large increase in operation scale shows significant promise for the Lextran technology. Additional development tests may assist Lextran in addressing all issues that arose at this scale.

Subtask 4.27 – Evaluation of the Multielement Sorbent Trap (MEST) Method at an Illinois Coal-Fired Plant

Program Area:	CRDP
Period of Performance:	6/1/13–9/30/14
Funding:	DOE: $192,665; Nonfederal: $347,578; Total: $540,243
EERC Subtask Manager:	John Pavlish
DOE Technical Monitor:	Barbara Carney
Nonfederal Partners:	CATM Affiliates Program, EPRI, ICCI, and Southern Illinois Power Company (SIPC)
Final Report:	Pavlish, J.H.; Thompson, J.S.; Dunham, G.E. *Subtask 4.27 – Evaluation of the Multielement Sorbent Trap (MEST) Method at an Illinois Coal-Fired Plant*; Final Report (June 1, 2013 – Sept 30, 2014) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2014-EERC-09-17; Energy & Environmental Research Center: Grand Forks, ND, Sept 2014.

In Subtask 4.27, the applicability and performance of the MEST method was evaluated for measuring trace metal and HCl emissions at two power plant units that burn Illinois Basin coal. Over the past two decades, emissions of mercury, nonmercury metals, and acid gases from energy generation have become the focus of regulatory rule making. On February 16, 2012, EPA promulgated MATS to reduce mercury, nonmercury metals, and HCl emissions from coal-fired power plants (2). The standard sets limits on mercury, nonmercury metal, and acid gas (HCl, and for oil units, hydrofluoric acid) emissions from new and existing coal- and oil-fired power plant units. After the compliance deadline (2015, or later if a waiver is given), coal- and oil-fired EGUs will have to measure and report emissions and maintain emissions below specified limits. The reference measurement method for halogens is EPA M26 (nonisokinetic) or M26A (isokinetic), wet-chemistry, impinger-based methods that are designed to collect both acid gas and halogen gas species present in flue gas. The reference method for mercury and nonmercury metal HAPs is EPA

M29, also an impinger-based method. There are a number of concerns regarding the use of EPA M26/26A and M29 to meet MATS requirements, including the following:

- The EPA methods are difficult to use, require highly trained personnel, and involve substantial preparation.
- The methods use toxic chemicals that are a concern for safety, shipping, and ultimate disposal.
- A very high level of QC is required, not only for sample analysis but for the sample-collecting activities.
- The detection limits for EPA M29 may not be adequate in some cases to measure accurately at the existing unit limits established under MATS.
- Inclusion of mercury in a M29 test creates a risk of contaminating the sample with Mn, because of the additional permanganate impinger that must be added to the sampling train.

As a potential alternative to EPA M29 and M26/26A, the EERC developed a MEST method with two separate sampling applications: one for metals (MEST-M) and one for halogens (MEST-H). A comparative study of the MEST-H method and EPA M26/M26A was performed for the two power plants. Sampling at the two units presented relatively high and low HCl emission levels, challenging the MEST-H over a wide range. A statistical analysis was used to compare the relative bias and precision of the two methods. Results of the comparison indicated no significant bias for HCl by MEST-H compared to M26A, based on EPA M301 criteria. At both units, the HCl emission measurements for each run showed excellent agreement between EPA M26A and the MEST-H method, generally within 5%–10%. The relative differences (RDs) for the paired MEST-H traps were generally less than 20% RD, with much of the data showing less than 10% RD. RA was less than 5%.

Redesign of trap and material selection has reduced background contributions of HCl from the sorbent material by a factor of over 10. Blank values are ~100 times lower than the MATS limit for new/reconstructed coal-fired units.

Comparative results between the MEST-M and M29 for Sb, As, Be, and Co show general agreement, and the difference is primarily due to M29 having a higher detection limit than MEST-M. Measured Sb, As, Be, and Co levels were relatively low at both units, with values at or below M29 detection limits. The MEST-M for these metals showed improved detection limits generally of a factor of 2 better than M29, resulting in concentrations that were approximately 50% of M29 detection values.

As seen at other plants, Cd, Cr, Pb, Mn, and Ni were shown to be much more variable, making comparison between MEST-M and M29 difficult. Measured values between the two methods were generally within 100%, with many of the values being within 50%. While precautions were taken to minimize trap Pb and Cd contamination, background contributions were still significant. Cr and Ni showed improved comparative results compared to previously sampled

plants. Comparatively, Mn values improved significantly with respect to previous measurements. Hg and Se showed comparable results for both MEST-M and M29 for both units, generally within 20%.

It is extremely difficult, if not impossible, to ensure MATS compliance measurement for all 11 of the trace elements using either M29 or the MEST-M method at the low level concentrations required by MATS. The two main reasons are high background values (Cr, Pb, Mn, and Ni) and limitations of instrumentation detection limits (Sb, As, Be, Cd, and Co). Longer sampling duration and larger sample volumes can improve the method detection proportionally but at the expense of increased time (cost) and risk.

Based on these data and conclusions from previous tests, The MEST-H method shows promise as an alternative to EPA M26 or 26A for measuring HCl at the limits for both existing and new/reconstructed coal-fired units. For the MEST-M method, additional research is still needed to explore possible longer sampling durations and/or selection of lower-background materials before the MEST-M method can be considered as a potential alternative method to M29.

Reference

1. National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units: Final Rule (Mercury and Air Toxics Standards [MATS]). 40 Code of Federal Regulations, Parts 60 and 63; *Fed. Regist*. **2012**, *77* (32), 9304.

Task 5.0 – Water Management and Sustainability

Subtask 5.1 – Optimization of Cooling Water Resources for Power Generation

Program Area:	CRD
Period of Performance:	7/1/08–12/31/09
Funding:	DOE: $140,000; Nonfederal: NA; Total: $140,000
EERC Subtask Manager:	D. Stepan
DOE Technical Monitor:	Andrea McNemar
Nonfederal Partners:	NA
Final Report:	Stepan, D.J., Shockey, R.E., Kalenze, N.S., Kurz, B.A., and Peck, W.D., 2009, Subtask 5.1 – optimization of cooling water resources for power generation: Final report (March 31 – October 31, 2009) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2009-EERC-12-07, Grand Forks, North Dakota, Energy & Environmental Research Center, December.

In Subtask 5.1, development continued on a regional DSS tailored to provide power generation utilities with an interactive assessment tool to address water supply issues that are essential when planning new or modifying existing generation facilities. The overall goal of the Web-based DSS was to integrate water and wastewater treatment technology and water law information with a GIS-based interactive map that houses or links to water quality and quantity databases.

Adequate supplies of quality water are critical to the existing and future power generation needs of the nation. While producing nearly 60% of the nation's annual energy needs, fossil energy production places a great demand on suitable and available water resources. Power production is comparable to irrigation in terms of annual water withdrawals in the United States, accounting for nearly 40% of those withdrawals. New economic development and population increases and shifts to water-scarce areas will create an even greater demand for fossil energy and further stress available water supplies.

The EERC has developed an interactive, Web-based DSS to provide power generation utilities with an assessment tool to address water supply issues when planning new or modifying existing generation facilities. The Web-based DSS integrates water and wastewater treatment technology and water law information with a GIS-based interactive map that links to state and federal water quality and quantity databases. The DSS includes sections that provide information on water law, water and wastewater treatment technologies, and conventional and nonconventional water resources, all of which are linked to other Web sites that provide in-depth information. This allows users to leverage and integrate knowledge of water and wastewater treatment technologies with the physical and spatial relationships of available water sources, competing uses, and current water demands.

In this subtask, the DSS was expanded from a three-state region, North Dakota, South Dakota, and Minnesota, to an eight-state region that includes North Dakota, South Dakota, Minnesota, Wyoming, Montana, Nebraska, Wisconsin, and Iowa. The expanded DSS provides a useful tool to an even larger audience, which is not just limited to those involved in power generation. It also benefits users from other industries, agriculture, and municipalities who are seeking new water resources or potential options for treatment and reuse of existing water supplies.

Subtask 5.2 – The Northern Great Plains Water Consortium

Program Area:	SNESS
Period of Performance:	7/1/08–12/31/12
Funding:	DOE: $3,045,837; Nonfederal: $4,987,681; Total: $8,033,518
EERC Subtask Manager:	Daniel Stepan
DOE Technical Monitor:	Arun Bose
Nonfederal Partners:	American Crystal Sugar, Cass County, City of East Grand Forks, City of East Grand Forks Water & Light, City of Fargo, City of Grand Forks, City of Moorhead, Grand Forks County Commission, Grand Forks County Water Board, Hess Corporation, NDIC, North Dakota Petroleum Council (NDPC), PPB, and University of Wyoming
Final Report:	Stepan, D.J., 2012, Subtask 5.2 – Northern Great Plains Water Consortium: Final report (July 1, 2008 – December 31, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291, EERC Publication 2012-EERC-12-18, Grand Forks, North Dakota, Energy & Environmental Research Center, December.

In Subtask 5.2, the NGPWC brought together key energy-producing and water-using entities in the northern Great Plains region to address issues related to water availability, reducing freshwater use, and minimizing the impacts of facility operations on water quality. The overall goal of this stakeholder-driven effort was to assess, develop, and demonstrate technologies and methodologies that minimize water use and reduce the discharge of water that has been impacted by energy technologies, including coal combustion, coal gasification, CBM, and oil and natural gas production and processing, along with investigations into water management synergies that exist between energy-producing entities and the customers they serve.

NGPWC undertook eight individual projects over the 5-year period of performance:

Bakken Water Opportunities Assessment – a two-phase project that investigated critical water supply and disposal issues in the Bakken shale oil play where advances in hydraulic fracturing have allowed the production of a projected 300 Bbbl to 400 Bbbl of original oil in place, the largest continuous accumulation of oil ever assessed by the U.S. Geological Survey. Phase 1 research on this project determined that there would be significant challenges for recycling fracturing flowback water because of very low water recovery rates (15% to 45% of the original volume of water used) and extremely high salinity levels (as high as 220,000 mg/L). Phase 2 research successfully demonstrated the economically competitive treatment of nonpotable saline groundwater for use as makeup water for hydraulic fracturing using reverse osmosis. Over 20 million gal of saline groundwater was treated to produce 14.4 million gal of high-quality permeate, a 72% recovery rate.

Recovery of Water from the Drying of LRCs – a project that investigated recovering water from the drying of high-moisture coals. This project identified the potential to recover up to 200,000 gal a day of high-quality water from GRE's lignite fuel enhancement system that dries up to 20,000 tpd of lignite. Water recovery was evaluated using three different techniques, but the highest and most economical recovery was assessed at a 30% average annual water recovery using a commercial ambient air heat exchange process, SPX Cooling Technologies' ClearSky™ technology.

Water Issues for Power Generation in the NGPWC Region – a project that identified critical water supply and use issues related to both existing and planned coal-fired power generation facilities in the NGPWC region. The project compiled data and information into the NGPWC's Water Resource DSS, a Web-based GIS-based interactive map that houses quantity and quality data for surface water resources, groundwater resources, and municipal and industrial wastewater treatment plant discharges greater than 1 MGD. State-level water law descriptions and contacts are provided to guide the user in water appropriations.

Energy–Water Nexus Documentary – a project that developed a half-hour documentary, "Water: The Lifeblood of Energy," in high-definition format on the energy–water nexus that highlights the key issues related to the interdependence of water and energy in the NGPWC region. The documentary has aired on public television in the PPB region that includes North Dakota; northwestern Minnesota; southern Manitoba, Canada, including the city of Winnipeg; northern South Dakota; and eastern Montana. A thousand DVD copies of the documentary were made available for distribution. The documentary is also viewable on the NGPWC Web page: www.undeerc.org/Water.

Water Issues in Carbon Capture – a project that was to investigate water usage for carbon capture during postcombustion and oxyfuel combustion. This project was subsequently removed from the overall program as efforts to secure the necessary cost share were unsuccessful.

Energy-Saving Opportunities in Water Treatment and Distribution – a project that investigated energy-saving opportunities for water treatment, including unit operations such as ozonation, and potential reductions in energy costs associated with water distribution. The project included laboratory testing of ozonation and UV light disinfection processes. Ozonation was found to be effective in controlling by-product formation during disinfection at a dose of 20 mg/L, with estimated costs of $1.4 to $2.2 million for a 4-MGD water treatment plant.

Testing of an Advanced Dry Cooling Technology for Power Plants in Arid Climates – Stage 1 – a project that demonstrated significant potential as a dry cooling alternative for power plants. Laboratory performance and optimization tests demonstrated the key operating concepts which led to continued process development and demonstration independent of NGPWC.

Critical Water Issues for Petroleum Refining – a project that investigated water supply and treatment issues faced by today's oil refineries that are processing increasingly lower cost crude oils and discounted refinery residues—heavier feedstocks, containing more sulfur and heavy metals—at a time when federal and state governments are considering increasingly more stringent environmental regulations for selenium, heavy metals, and nutrients in wastewater.

Subtask 5.3 – Water and Energy Sustainability and Technology (WEST)

Program Area:	IEP
Period of Performance:	10/1/08–9/30/10
Funding:	DOE: $1,000,000; Nonfederal: $250,000; Total: $1,250,000
EERC Subtask Manager:	Bruce Folkedahl
DOE Technical Monitor:	Barbara Carney
Nonfederal Partners:	ATCO Power, Baker Hughes, Midwest Energy Generation, Minnesota Power, SaskPower, and TransAlta
Final Report:	Folkedahl, B.C.; Martin, C.L.; Dunham, D.J. Subtask 5.3 – Water and Energy Sustainability and Technology; Final Report (Oct 1, 2008 – Sept 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-09-10; Energy & Environmental Research Center: Grand Forks, ND, Sept 2010.

In Subtask 5.3, water capture technologies in a carbon capture and sequestration system were evaluated and a complete systems analysis was performed on the process to determine potential water minimization opportunities within the entire system. To achieve that goal, a pilot-scale LDDS was fabricated and tested in conjunction with a coal-fired combustion test furnace outfitted with CO_2 mitigation technologies including the options of oxy-fired operation and postcombustion

CO_2 capture using an amine scrubber. Important factors in the design were the flue gas flow rate entering the absorber as well as the temperature of the gas entering the LDDS.

Shakedown testing with both oxy-fired and CO_2-scrubbing configurations was conducted along with four sets of extended-duration tests using the LDDS to recover moisture following the CO_2 scrubber. The process gas stream for these tests was a coal-derived flue gas that had undergone conventional pollutant control (particulates, SO_2) and CO_2 capture with an amine-based scrubber.

The water balance data from the pilot-scale tests show that the packed-bed absorber design was very effective at capturing moisture down to levels that approach equilibrium conditions. Product water samples from the pilot-scale LDDS were routinely collected during test runs and analyzed for suspected contaminants. Compared to previous studies of moisture recovery from conventional coal flue gas, which were slightly acidic, the product water reclaimed from the CO_2 scrubber exhaust consistently had a high, basic pH. This is most likely a result of trace carryover of amine solution from the upstream CO_2 scrubber.

An energy balance for the pilot-scale LDDS shows that very little preheating of the working fluid was accomplished in the condensing flue gas heat exchanger and, therefore, electric heat input was required for the majority of energy into the system. As a result, it was not possible to operate the system autothermally: that is, without external heat input. Examination of the operating conditions for the flue gas heat exchanger suggest it is unlikely that significant improvements could be made; however, the electric heat input could be reduced by installing a solution heat exchanger. In this heat exchanger, the hot, strong solution leaving the evaporator would be used to preheat the incoming weak solution.

When the LDDS was used to recover moisture from a concentrated CO_2 stream, CO_2 was partially absorbed because it is slightly soluble in aqueous solution. During shakedown tests of the pilot-scale LDDS under oxy-fired conditions, the desiccant solution was neutralized with a bed of $CaCO_3$, and in extreme cases, $Ca(OH)_2$ was added to raise pH.

In terms of the most productive applications for the LDDS, higher-temperature, saturated gas flows offer the most promise. Not only does the maximum capture potential increase for the LDDS with increasing temperature, but the available saturated water content increases dramatically with temperature. For the plant configurations of interest in this work, that is, oxy-fired or conventional combustion with CO_2 capture, LDDS moisture recovery may be at a disadvantage since the process gas temperatures will be lower to accommodate either downstream CO_2 compression equipment or upstream amine-based scrubbers. Lower temperatures imply lower moisture content for recovery, which would tend to increase the levelized cost of LDDS water production.

The LDDS can feasibly recover a higher percentage of water than ambient-temperature condensation and can use low-temperature recovered heat for input energy, but it is a capital-intense approach. Novel integration strategies are needed to distribute the capital expenses among several power plant functions in order to make the LDDS concept more attractive. Identified strategies include making the absorber multipurpose: for example, moisture absorption and

polishing SO_2 control, recovering moisture from multiple process streams using common evaporator and condenser components and, possibly, sharing the plant's steam condenser to recover product water.

Subtask 5.4 – Novel Thermal Storage for Power Plants

Program Area:	CRD
Period of Performance:	7/1/09–6/30/10
Funding:	DOE: $60,000; Nonfederal: NA; Total: $60,000
EERC Subtask Manager:	Chris Martin
DOE Technical Monitor:	Steven Seachman
Nonfederal Partners:	NA
Final Report:	Martin, C.L. Subtask 5.4 – Novel Thermal Storage for Power Plants; Final Report (July 1, 2009 – June 30, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-06-04; Energy & Environmental Research Center: Grand Forks, ND, June 2010.

Under Subtask 5.4, a feasibility study was conducted on a novel EERC method for large-scale thermal energy storage that could be used to benefit the peak operating efficiency of Rankine-based power plants. The concept under investigation is a method to augment the cooling needs of power plants without consuming additional water resources. Instead, supplemental cooling water is harvested directly from the ambient air by recovering atmospheric moisture. Water collection takes place during the early-morning hours when ambient temperatures are lowest and relative humidity is typically at a maximum. The harvested water is stored until the next afternoon, when ambient temperatures are higher, and evaporated to provide peak cooling.

The thermal storage concept investigated appeared to have several possible benefits for thermal power plants by affecting one or more of the following interrelated factors: plant efficiency, heat rejection capacity, and heat rejection temperature. To effectively consider the impact of thermal storage on the overall process, a simulation embedded with these interrelationships was created and used to estimate the performance of the thermal storage system. At the core of the process simulation was an estimate of the heat and mass transfer performance of the thermal storage device's ambient air contactor. A numerical model representing the geometry of the working fluid–ambient air contacting process of the experimental system was created and used to simulate the interchange of moisture and thermal energy between the two process streams. The simulation was validated with data generated by the experimental system.

The validated simulation of the thermal storage system was used to compute the continuous performance of the system and to estimate its economic impact. Hypothetical plant sites were selected across the United States, and local average climate data were used to size and simulate the performance of the thermal storage concept. However, none of the cases evaluated appear to be particularly attractive investments, especially in light of the fact that there are other options for restoring full power output such as increasing the fuel feed rate. This economic analysis suggests that the thermal storage concept as originally envisioned is not a promising approach unless the

capital costs can be reduced. However, the technology will always be capital-intensive, given the large quantities of thermal energy that need to be transferred and stored.

Another possibility for the technology is to serve as the primary heat rejection device for a power plant instead of just augmenting the performance of an air-cooled condenser (ACC). Simulations were run to compare the performance of a cooling system based on the EERC's thermal storage concept to conventional options of wet recirculating cooling and an ACC. Results of this analysis suggest that the wet recirculating system has a capital cost advantage compared to the other two options, and in areas where water is available, this cooling system will typically be the best design choice for large-scale heat dissipation. However, in areas without sufficient water, the choice would be restricted to the EERC-based system and an ACC, and at this stage of estimation, it appears that the EERC system would have a clear cost advantage.

The EERC is currently pursuing intellectual property protection for the concept and is seeking industrial support for continued development of an alternative dry cooling technology based on the design of the EERC's thermal storage system.

Subtask 5.5 – Technological Synergies for Recovery of Organic Pollutants from a Coal Seam at Garrison, North Dakota – Phase 2: System Operation and Performance Monitoring

Program Area:	CRDP
Period of Performance:	4/1/09–12/31/11
Funding:	DOE: $238,335; Nonfederal: $424,635; Total: $662,970
EERC Subtask Manager:	Jaroslav Solc
DOE Technical Monitor:	Steven Markovich
Nonfederal Partner:	Farmers Union Oil Company
Final Report:	Solc, J.; Botnen, B.; Knutson, R. *Subtask 5.5 – Technological Synergies for Recovery of Organic Pollutants from a Coal Seam at Garrison, North Dakota*; Final Report (April 1, 2009 – Dec 31, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-12-02; Energy & Environmental Research Center: Grand Forks, ND, Dec 2011.

In Subtask 5.5, remediation activities were conducted on hydrocarbon-contaminated soils and groundwater associated with gasoline release at the Farmers Union Oil Cenex station in Garrison, North Dakota. A proactive remedial approach was required to reduce high contaminants of concern (COC) levels in the source and impacted areas and to eliminate long-term health risks associated with contaminant migration to water-bearing zones used as a regional water supply source.

Based on complex geotechnical conditions, the implemented remedial strategy was based on contaminant recovery and in situ degradation using an innovative combination of 1) thermally enhanced soil vapor extraction (SVE) in the source areas and 2) multiphase extraction supporting SVE in saturated impacted areas. The acceleration of COC recovery in hot spots was achieved by

thermal enhancement/hot-air injection conducted simultaneously with the operation of the SVE system. The operational principle was based on controlled hot-air circulation between injection and extraction wells to accelerate in situ COC volatilization and stripping alternatively using the same wells as either extraction or injection points.

A total of 431,002 gal (1072 m^3) of groundwater and 368.7 million ft^3 (6.5 million m^3) of contaminated soil vapor have been extracted from both well fields between November 13, 2008, and December 16, 2009, resulting in the removal of over 25,781 lb (11,694 kg) of vapor-phase hydrocarbons and an additional 1.8 lb (0.8 kg) from the treated groundwater. The mass of recovered contaminant equals approximately 4120 gal of product.

Groundwater-sampling results indicate that average sitewide contaminant reduction of 90% was achieved for individual monitoring wells. The successful operation of recovery systems reduced environmental and health risks associated with the occurrence of separated and dissolved-phase contaminants in the regional aquifer. Based on environmental monitoring results and improving site conditions, NDDH approved termination of the active remediation effort in the source area and initiation of site abandonment activities.

Subtask 5.6 – Design and Pilot Plant Studies of Water Minimization Technology

Program Area:	IEP
Period of Performance:	10/1/10–11/30/12
Funding:	DOE: $962,000; Nonfederal: $254,450; Total: $1,216,450
EERC Subtask Manager:	Bruce Folkedahl
DOE Technical Monitor:	Barbara Carney
Nonfederal Partner:	GEA Heat Exchangers, Inc. (GEA)
Final Report:	Folkedahl, B.C.; Leroux, K.M.; Jensen, R.R.; Martin, C.L.; Kalenze, N.S.; Richter, J.J.; Ziman, J.J.; Jorgenson, K.J.; Martin, K.E.; Palmiscno, K.J.; Gleich, A.F.; Gregasz, A.; Bannerth, C.; Szlavik, M.; Lohasz, M.; Szabo, Z.; Balogh, A.; Zekovich, A.; Smith, A. *Subtask 5.6 – Design and Pilot Plant Studies of Water Minimization Technology*; Final Report (Oct 1, 2010 – Nov 30, 2012) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2012-EERC-11-15; Energy & Environmental Research Center: Grand Forks, ND, Nov 2012.

In Subtask 5.6, a first-of-its-kind hybrid condenser for cooling systems at electricity generation facilities was constructed and tested to further reduce water consumption beyond the current capabilities of hybrid cooling systems. Thus the goal of this project was to determine the technical viability of the hybrid condenser for economically decreasing water requirements in electricity generation. The objectives were to conduct a technical literature review of state-of-the-art cooling systems; design, engineer, and construct a pilot-scale hybrid cooling system that could be used to elucidate pathways to greater efficiency and lower water use at power plants; generate sufficient subscale test data to assess the process feasibility; and evaluate merits for commercialization of the hybrid condenser.

Water conservation efforts at utilities are focused on cooling methods and technologies since a majority of water used in coal-fired power plants is to make up cooling water losses: ~5% plant processing, ~10% flue gas exhaust, and ~85% evaporative cooling. Cooling systems are generally categorized as once-through, wet/open-loop, dry/closed-loop, and hybrid. Once-through cooling was formerly the industry standard as water was taken from a nearby resource to pass through steam condensers and returned to the source with little water consumed or evaporated; however, high water withdrawals at the intake structure (~30,000 gal/MWh) and elevated temperatures at the discharge can negatively impact aquatic ecosystems, resulting in EPA regulation and restriction of these systems. Wet cooling systems have thus replaced once-through cooling by using evaporative cooling equipment that withdraws significantly less water (~2.5%) than once-through cooling. However, nearly all withdrawn water is consumed in wet cooling systems because of evaporative losses. Dry cooling options reject heat directly to the atmosphere, with air-cooled equipment eliminating water consumption from cooling activities. Although these systems are gaining some industry interest, they require significantly greater capital investment compared to conventional wet systems and are limited in cooling efficiency by the ambient dry-bulb temperature, an issue for arid regions where peak demand occurs during hot summer months.

Therefore, hybrid systems are emerging in the industry to benefit from the advantages of both wet cooling (greater cooling efficiencies, lower capital) and dry cooling (no water consumption); they generally have a lower capital cost than a completely closed loop system and use less water than a completely open loop system. However, current hybrid systems have two separate operating systems, often including separate condensers or condenser units. The literature review thus supported the novelty of the hybrid condenser among state-of-the-art cooling technologies.

The pilot test system, designed to supply and condense about 3 MMBtu/hr steam, was built to test the operation of a small-scale model of the hybrid condenser design. Steam generated at the University of North Dakota (UND) coal-fired steam plant was used to simulate power plant turbine exhaust. Since it is generated at high temperature and pressure, a desuperheater and vacuum pump were needed to bring the steam down to the lower temperature and vacuum conditions typical of turbine exhaust. The vacuum pump aided in trimming system conditions, specifically air ingression, which affects steam condensation efficiency and could be highly variable because of the small size of the pilot system. The model hybrid condenser integrated the operations of a direct-contact jet condenser (used in dry/closed-loop cooling applications) and a surface condenser (used mainly in wet/open-loop cooling applications) to affect condensation. The closed-loop stream provided cooling water to jet sprayers at the top of the condenser body, condensing the steam as it entered via direct contact, then flowed over surface condensing tubes to ensure complete condensation of any remaining steam. Condensate was pumped back to the UND steam system, and the cooling water was pumped to a heat exchanger, which simulated a dry cooling tower to remove the heat transferred during steam condensation before returning to the direct-contact jet section of the hybrid condenser. The open-loop stream provided cooling water to the surface condensing tubes and was then pumped to a commercial-grade wet cooling tower to remove any heat transferred before returning to the hybrid condenser. A data acquisition unit allowed for manual control of system operations and recorded all data generated.

Results showed the novel hybrid condenser design has the potential to significantly reduce overall investment costs up to 30% compared to all-dry/closed-loop cooling technology, decrease

water consumption up to 80% compared to conventional wet/open-loop cooling systems, and increase performance compared to similar hybrid systems. The hybrid condenser promotes synergy between wet and dry approaches to cooling, improving cooling efficiency and requiring lower cooling water flow rates, thus decreasing operational and maintenance expenses as well as increasing water savings over existing commercial hybrid systems currently in practice.

There is a growing market for the hybrid condenser at existing power plants with strictly wet/open-loop cooling systems where water resources have become limited. The costs of current hybrid systems are significant, requiring installation and operation of a separate dry/closed-loop cooling system to incorporate both technologies. The footprint of any added infrastructure at an existing facility is crucial to ensure the system can be easily integrated into ongoing operations within the confines of the land currently owned by the facility. Retrofitting a closed-loop condenser section directly in line (e.g., above or adjacent) with the existing open-loop condenser to effectively create a hybrid condenser or replacing it entirely with a new hybrid condenser reduces footprint and capital costs by eliminating the need for a separate closed-loop condenser. The synergy promoted by the hybrid condenser would also provide decreased operational costs and improved water reduction compared to conventional hybrid systems. Therefore, the ability of the hybrid condenser to be retrofitted into the existing layout of these power plants and the resulting water savings realized during operation make the hybrid condenser an attractive solution.

Subtask 5.7 – Sediment Pore Water PAH-34 Method Validation and Field Demonstration

Program Area:	CRDP
Period of Performance:	9/1/09–8/31/10
Funding:	DOE: $116,015; Nonfederal: $215,625; Total: $331,640
EERC Subtask Manager:	Steven Hawthorne
DOE Technical Monitor:	Barbara Carney
Nonfederal Partners:	AECOM and GEI Consultants
Final Report:	Hawthorne, S.B. *Subtask 5.7 – Sediment Pore Water PAH-34 Method Validation and Field Demonstration*; Final Report (July 1, 2009 – Aug 31, 2010) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2010-EERC-08-16; Energy & Environmental Research Center: Grand Forks, ND, Aug 2010.

Subtask 5.7 involved a round-robin study to validate ASTM provisional Method D7363. Risk assessment models used by state and federal regulatory agencies for polycyclic aromatic hydrocarbon (PAH)-contaminated soils and sediments frequently require cleanup of a contaminated site to below ambient background levels. Many studies have demonstrated that PAHs become increasingly less available as they age in the environment (especially in the presence of high organic carbon and soot carbon). Application of these ideas in the regulatory framework has been inhibited by the lack of rapid and accurate laboratory tests that can mimic relevant organism uptake upon exposure to PAH-contaminated materials in the environment.

In previous investigations, a solid-phase microextraction (SPME) method was developed to measure bioavailable (freely dissolved) pore water concentrations. In subsequent studies on ca. 30 industrial sites including more than 250 sediment samples, the EERC clearly demonstrated that the SPME technique greatly improves toxicity predictions over present regulatory equilibrium partitioning models based on sediment concentrations. These field trials continued to demonstrate the ability of the SPME pore water method to accurately predict the toxicity of PAHs to benthic organisms and to show that present regulatory models greatly overpredict toxicity, with the result of unreasonable and unnecessary cleanup criteria being applied to most sites.

While the scientific community has largely accepted the superiority of measuring dissolved concentrations over measuring sediment PAH-34 concentrations to predict biological effects and determine proper mitigation scenarios, the widespread implementation and regulatory acceptance of the EERC's SPME method for dissolved PAH-34 requires that the method be accepted by a recognized governing body such as ASTM so that it can be used by environmental contract labs and that it shows good robustness when subjected to rigorous field studies. To that end, a draft method (based only on EERC data) was submitted to ASTM and accepted by that body as a provisional ASTM Method D7363 in 2007.

The next step to full acceptance was achieved under Subtask 5.7 by performing a round-robin evaluation with seven operators in five different laboratories, including three environmental contract labs and two academic labs. The EERC prepared and distributed all solutions required by the study to all participating labs. Each lab and operator was required to successfully obtain calibration curves and blank results that met the ASTM QA criteria stated in provisional Method D7363 before proceeding with the study. Each lab and operator was also required to successfully analyze an unknown "test" sample prepared from a coal tar and report the results to the EERC for evaluation. Based on the test sample, it was necessary to correct incorrect calculations for some operators and to advise on proper integration of the complex isomeric alkyl clusters (and to eliminate nontarget interferences) for the majority of operators. Fortunately, these training steps were successful and also provided valuable changes needed to clarify the final ASTM method. The same coal tar was used to generate six concentrations needed for "Youden Pair" statistical sets required by ASTM. The surrogate recovery solutions required were also prepared. The EERC distributed these materials as well as calibration and internal standard solutions to all participating labs.

The round-robin study appears to be a success based on ASTM criteria. An initial presentation of the round-robin data to the ASTM committee presented in June 2010 was well accepted; however, the statistical evaluation had not yet been performed. The final data and evaluation report were submitted to the committee, with balloting for final acceptance in January 2011.

The robustness of the methodology under "contract lab" conditions was evaluated during an extensive field study including 62 sediments. Both the pore water PAH-34 method (ASTM D7363) and the associated methods, including sediment PAH-34, TOC, and "soot" or "black" organic carbon (SOC), were performed by technician-level chemists as would be done under typical contract lab conditions. All criteria stated in ASTM D7363 as well as the EERC's QA/QC document covering other methods that are "nonstandard" were met with no exceptions. These

criteria governing sample-holding times, acceptable method blanks, calibration linearity and reproducibility, and surrogate recovery were met in 100% of the procedures on all 62 sediments, thus demonstrating the ability of the methods to perform for large field studies under contract lab conditions.

Subtask 5.8 – Electrochemically Promoted Microbial Hydrogen Production from Biomass and Wastewater

Program Area:	CRD
Period of Performance:	6/15/10–6/30/11
Funding:	DOE: $100,000; Nonfederal: NA; Total: $100,000
EERC Subtask Manager:	Dingyi Ye
DOE Technical Monitor:	Darryl Shockley
Nonfederal Partners:	NA
Final Report:	Ye, D. *Subtask 5.8 – Electrochemically Promoted Microbial Hydrogen Production from Biomass and Wastewater*; Final Report (June 15, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-25; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

In Subtask 5.8, a project was undertaken to develop a "green" energy technology that uses the electrochemically promoted dark fermentation process to produce hydrogen and water from agricultural and food-processing wastes and wastewaters for direct liquefaction of coal. Direct conversion of coal to liquids by the hydrogenation process requires a large quantity of hydrogen. Hydrogen itself is a clean energy and can be used in stationary fuel cells or fuel cell vehicles. It is well known that hydrogen can also be produced from biomass via microbial fermentation. Despite *the global increase in demand for hydrogen as well as the global abundance of biomass, to date*, little hydrogen is produced from this renewable source. The major issue is that the yield of microbial hydrogen production from biomass is low, and the reaction always results in some "dead end" products. Recently, it has been reported that this thermodynamic barrier can be overcome with electrochemical promotion whereby the modified fermentation process would significantly increase hydrogen yield and expand the spectrum of renewable hydrogen sources, thereby contributing to meeting the overall hydrogen demand. Research on this novel topic is in the very early stages, and more efforts are needed so that this promising protocol may be fully developed into a mature clean energy technology.

Three types of local wastewater were investigated: a sugar industry wastewater from ACS, a potato-processing wastewater from JR Simplot Company, and a municipal wastewater from the Grand Forks Water Treatment Plant (GFWTP). Hydrogen was produced from both the sugar industry wastewater and the potato-processing wastewater, indicating the potential of these wastewaters for microbial hydrogen fermentation. Hydrogen-producing bacteria were enriched from these two wastewaters, and the activities were successfully maintained through monthly 5% transfer.

Effluent from a municipal wastewater treatment plant was also assessed. Results of the GFWTP wastewater experiment evidenced that this municipal wastewater sample contained low (or no) level of hydrogen-producing bacteria; it was also low in organic carbon because it had undergone aerobic biological treatment before sampling. These experimental results showed that this water (Grand Forks municipal wastewater after aerobic biological treatment) is not suitable for further microbial hydrogen fermentation.

The effects of temperature, oxygen, and nutrients were examined to determine their impacts on the microbial hydrogen fermentation process. The temperature experimental results showed that at 20°C, the hydrogen production rate was slower than at 30° and 35°C; however, no significant difference was noted in hydrogen production between 30° and 35°C. It appeared that the presence of air at the beginning stage slightly delayed hydrogen production but did not affect the total amount of hydrogen production. Addition of nutrients to ACS and Simplot wastewater did not stimulate hydrogen production, suggesting that these wastewaters were rich in natural substances, which usually comprise a wide spectrum of nutrients.

Compared to microbial hydrogen fermentation without electrochemical promotion, electrochemical assistance significantly enhanced the hydrogen fermentation. This conclusion was confirmed by experiments using simulated wastewater consisting of both acetate or glucose plus starch solutions as the carbon and energy sources and experiments using ACS or Simplot wastewaters. In all of these experiments, the electrochemically promoted microbial hydrogen fermentation produced several times more hydrogen than those produced by microbial fermentation without electrochemical assistance. These results not only proved that electrochemical assistance was capable of significantly enhancing microbial hydrogen fermentation, but also demonstrated the application potential of this technology in recovering the clean energy (H_2) from agriculture waste and organic-rich wastewaters.

Subtask 5.9 – Finalizing ASTM Method and SRM Support

Program Area:	CRDP
Period of Performance:	11/1/10–6/30/11
Funding:	DOE: $30,273; Nonfederal: $56,250; Total: $86,523
EERC Subtask Manager:	Steven Hawthorne
DOE Technical Monitor:	Barbara Carney
Nonfederal Partners:	Alcoa Technology and GEI Consultants
Final Report:	Hawthorne, S.B. *Subtask 5.9 – Finalizing ASTM Method and SRM Support*; Final Report (Nov 1, 2010 – June 30, 2011) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2011-EERC-06-07; Energy & Environmental Research Center: Grand Forks, ND, June 2011.

Under Subtask 5.9, revisions to ASTM Method D7363 were completed to improve the method based on the round-robin laboratory experience conducted under Subtask 5.7. PAHs are among the most prevalent industrial organic contaminants in urban sediments. There are many diverse sources of PAHs in contaminated sediments related to the use of fossil fuels, including

pyrogenic sources such as coal tars produced during manufactured gas plant activities and the subsequent use of coal tar products by related industries\, as well as petrogenic sources such as the spill of crude oil in the Gulf of Mexico. Unfortunately, both federal and state regulatory decisions on mitigating sediments impacted by PAHs are based on outdated models to predict the bioavailability of PAHs. It is commonly recognized in the scientific literature that these models most often overpredict the impacts of PAHs and lead to costly and unnecessary remediation activities.

Previous EERC investigations have demonstrated that the measurement of PAH-34 (18 parent PAHs and 16 groups of alkylated isomeric clusters) that are freely dissolved in sediment pore water is far superior to predict the bioavailability of sediment PAHs than the current regulatory model. Regulatory acceptance and widespread application of the EERC's approach to measure dissolved PAH-34 PAH concentrations for predicting PAH bioavailability will require that the method be formally accepted by a regulatory body as a standard method that can be used by conventional contract laboratories so that the method is widely available and monitored by QA and record-keeping guidelines suitable for the regulatory format. In addition, it is important to demonstrate that the method is capable of long-term reliability for monitoring remediation activities for complex field sites.

Under Subtask 5.7, the EERC successfully conducted a round-robin multilaboratory study required by ASTM in order to gain final acceptance of ASTM D7363. This method, developed at the EERC, will be the first and only method to measure the dissolved concentrations of PAH-34 accepted by regulatory bodies and available for use by certified contract laboratories. The purpose of activities under Subtask 5.9 was to correct deficiencies in the draft method that became apparent during the multilaboratory study and to collaborate with the National Institute of Standards and Technology (NIST) to certify a coal tar–petroleum nonaqueous-phase liquid (NAPL) used in the multilaboratory round-robin study as a standard reference material (SRM), thus fulfilling a critical need for the finalized ASTM method to be transferred to certified contract labs.

During Subtask 5.9, the EERC completed revising ASTM Method D7363 to improve the method based on the round-robin laboratory experience. Revisions to the method were also presented to the ASTM committee at its January meeting. The most important change to the ASTM method is the addition of the mixed coal tar–petroleum NAPL to be used as a calibration standard for labs to determine the relative response factors for alkyl PAHs. This change was made in order to solve laboratory procedural issues that surfaced during the multilaboratory round-robin validation studies. The EERC provided sufficient quantities of the NAPL to NIST for it to prepare the bulk SRM materials, and NIST completed the preparation of several thousand vials of the new SRM 1991. NIST provided the EERC with sample vials of the SRM, and the EERC performed experiments to validate the use of the new SRM for calibration of the alkyl PAH isomeric clusters as is mandated in the revised ASTM method. Detailed conversations with NIST on the approaches needed to certify the alkyl PAHs in the SRM were also held, and the EERC provided analytical support to NIST on its initial stages of certification.

Formal balloting of the revised method by the ASTM committee was successful, with only minor formatting changes, and one procedural clarification requested. All changes were made to

the method as requested, and formal acceptance and publication of ASTM D7363 was anticipated to occur in the late summer or early fall of 2011.

Subtask 5.10 – Testing of an Advanced Dry Cooling Technology for Power Plants

Program Area:	IEP
Period of Performance:	10/1/12–9/30/13
Funding:	DOE: $309,000; Nonfederal: $187,500; Total: $496,500
EERC Subtask Manager:	Christopher Martin
DOE Technical Monitor:	Barbara Carney
Nonfederal Partner:	University of Wyoming (through Wyoming Clean Coal Technologies Research Program)
Final Report:	Martin, C.L.; Pavlish, J.H. *Subtask 5.10 – Testing of an Advanced Dry Cooling Technology for Power Plants*; Final Report (Oct 1, 2012 – Sept 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-09-09; Energy & Environmental Research Center: Grand Forks, ND, Sept 2013.

Subtask 5.10 involved the testing of an advanced dry cooling technology for power plants. The EERC is developing a novel dry cooling technology to meet the cooling needs of power plants located in arid environments. This technology is intended to address the key shortcomings of conventional dry cooling technologies: high capital cost and degraded cooling performance during daytime temperature peaks. The key feature of desiccant dry cooling (DDC) technology is the use of a hygroscopic working fluid—a liquid desiccant—as a heat-transfer medium between a power plant's steam condenser and the atmosphere. This configuration affords several advantages for overall cooling system performance.

The overall goal of this project was to accurately define the performance and cost characteristics of DDC to determine if further development of the concept is warranted. To achieve this goal, necessary supporting project efforts were divided into several activities, including experimental performance measurement of a DDC system, extrapolation of the measured results to full-scale power plants, development of an economic model for DDC and, finally, case study calculations to compare the features of DDC to the conventional cooling options of wet recirculating cooling and an ACC.

The resulting performance and economic models were used to evaluate case studies that were based on cooling a 300-MWe-net coal power plant for three different locations: Gillette, Wyoming; Atlanta, Georgia; and Phoenix, Arizona. The case study calculations indicate that DDC consistently maintained a lower annual cooling system cost compared to an ACC. Annual cooling costs for DDC averaged 60% of those of an ACC for the evaluated cases. Parasitic power requirements for DDC were also estimated to be lower, averaging 65% of those for a comparable ACC. Compared to wet recirculating cooling, the annual costs for DDC were within ±10% of the comparable wet system including the energy penalties associated with lost power production with the desiccant system. The breakeven cost of water for DDC ranged from a low of $1.72/kgal for Atlanta to a high of $3.35/kgal for Phoenix for the specific assumptions used.

Regarding the potential environmental impacts of DDC, experimental testing supports the hypothesis that DDC can be an environmentally benign cooling option. The key environmental concern, carryover of desiccant, appears to be manageable with proper design and operation of the cooling system. Measured drift rates were determined to be less than 0.00006% of the circulating working fluid rate. However, it is desirable to demonstrate an even lower limit for drift to avoid potential particulate emission limits that are currently imposed on conventional wet cooling towers.

This project has also highlighted the key technological steps that must be taken in order to transfer DDC into the marketplace. To address these issues and to offer an extended demonstration of DDC technology, a next-stage project should include the opportunity for outdoor ambient testing of a small DDC cooling cell.

Task 6.0 – Strategic Studies

Subtask 6.1 – Strategic Studies

Program Area:	CRD, CS, and CC
Period of Performance:	7/1/08–5/31/15
Funding:	DOE: $643,000; Nonfederal: NA; Total: $643,000
EERC Subtask Manager:	John Harju
DOE Technical Monitor:	I. Andrew Aurelio
Nonfederal Partners:	NA
Final Report:	Erickson, T.A.; Harju, J.A.; Steadman, E.N.; Holmes, M.J. *Subtask 6.1 – Strategic Studies*; Final Report (July 1, 2008 – May 31, 2015) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2015-EERC-05-01; Energy & Environmental Research Center: Grand Forks, ND, May 2015.

In Subtask 6.1, 7 years of research was completed that focused on fossil energy technology development and demonstration. The goal of this subtask was to provide support for small, focused efforts that address some of the most pressing needs faced by fossil energy. The wide range of topics addressed reflects the dynamic nature of the fossil energy industry. Since work began in this subtask, the energy picture in the United States has changed dramatically. Coal use for electrical generation has decreased from 48.3% in 2008 to 38.9% in 2014 (1). The bulk of this new demand has been offset by an increase in the use of natural gas for electrical generation, which has increased from 21.5% to 27.5% in the same time period, with a peak in 2012 of 30.4%, while coal was 37.5%. Over the same time frame, domestic oil production has grown from approximately 5 MMbbl/day in 2008 to 9 MMbbl/day in 2014. The mounting environmental pressures that coal is facing, including significant pressure to address climate change concerns, combined with the technology-based increases in domestic oil and gas production are the primary drivers for these dramatic shifts in the energy picture in the United States and world. DOE has been a key partner in the development of the technologies that are changing the energy picture, and the EERC's strong partnership with DOE over three decades has been based on a firm foundation of practical applied

research that enjoys the support and partnership of industry, resulting in rapid and efficient deployment of new technologies.

To support a significant number of different activities considered within all of the EERC's research contracts with NETL, a subtask was created to focus on small research efforts that came up throughout the year that would support an existing DOE–EERC project or would help to develop a new concept for potential inclusion in future efforts. The Strategic Studies topics that were investigated herein focused on the development of small amounts of key data and information that will attract the interest of the fossil energy research and industrial community.

Two activities were conducted under Subtask 6.1:

- Activity 1 – Systems Engineering evaluated alternative processes and technologies to determine if research activities were worthy of additional investment. For technologies near commercialization, work involved the optimization of configurations or operating conditions, validation of laboratory and pilot plant data, and scale-up assistance to ensure that appropriate data were obtained and that the product cost and quality met the requirements of industry partners or other users.

- Activity 2 – Ministudies, included performing small paper studies on topics of interest to DOE, particularly emerging concepts and technologies that may affect domestic energy supplies.

Over the last 7 years, under Activity 2, 20 ministudies were conducted. These efforts ranged from quick experiments to gain fundamental knowledge to support a current effort, to literature reviews, to a few larger engineering efforts. In the last 4 years, the studies have focused exclusively on CCS.

The range of ministudies projects conducted can be classified into three broad categories: Novel Carbon Capture Studies, Novel Carbon Storage Studies, and Preliminary Engineering Studies. The following is a list of the research projects conducted, classified as described above:

<u>Novel Carbon Capture Studies</u>

- Development of Novel Material Applications for Improving Performance of Distributed Liquid Production Process – Material Selection and Evaluation

- Synthesis of Hydrocarbon Fuel from Flue Gas CO_2 Using Renewable Energy Sources

- Economic Evaluation of CO_2 Capture Processes Using Aspen Icarus Process Evaluator

- Preliminary Evaluation of Using Supercritical Carbon Dioxide and Waste Organic Acids to Acidify Water for the Production of Simple Sugars from Switchgrass

- CO_2 Capture from Algae – Use as a Fish Food/Dietary Supplement

- Application and Use of Advances in Amines for Natural Gas Sweetening
- Investigation of Vapor-Phase Emissions from Amine-Based CO_2 Capture
- Optimization of Technology Development in the Context of Industrial CO_2 Sources
- Modification of Amine Solvent Stripping Process to Reduce Energy Input of CO_2 Capture
- CO_2 Capture Using Treated Activated Carbon and Electrically Driven Thermal Swing Adsorption Regeneration
- Review and Modeling of Precombustion Capture of CO_2 from Natural Gas-Fired Plants
- Assessment of the Operational Integration of CO_2 Capture at a Coal-Fired Utility

Novel Carbon Storage Studies

- Investigation of North Dakota Clays for Making Ceramic Proppants
- Evaluation of Clay-Based Cenospheres for Use in Hydraulic Fracturing
- Electrical Thermal Swing Adsorption Testing to Enhance CO_2 Flood Efficiency and Natural Gas Liquids Separation
- Measurement of CO_2 Adsorption Isotherms for Clays
- Development of an Analytical Approach to Differentiate Between Different Corrosion and Scale-Forming Mechanisms

Preliminary Engineering Studies

- Evaluation of Electric Vehicles and Other Fossil-Based Technologies as Near-Term Solutions to Reducing Foreign Oil Imports
- Zero-Energy Buildings
- Preliminary Evaluation of Non-Pt Alkaline Methanol Fuel

Reference

1. U.S. Energy Information Administration. Short-Term Energy Outlook. www.eia.gov/ forecasts/steo/pdf/steo_ full.pdf (accessed May 2015).

Subtask 6.2 – Investigation of Two CO_2 Capture Strategy Concepts

Program Area:	CRD
Period of Performance:	11/1/16–8/31/17
Funding:	DOE: $58,800; Nonfederal: NA; Total: $58,800
EERC Subtask Manager:	John Kay
DOE Technical Monitor:	I. Andrew Aurelio
Nonfederal Partners:	NA
Final Report:	Kay, J.P.; Jensen, M.D.; Fiala, N.J.; Patel, N.M. *Subtask 6.2 – Investigation of Two CO_2 Capture Strategy Concepts*; Final Report (Nov 1, 2016 – Aug 31, 2017) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2017-EERC-09-06; Energy & Environmental Research Center: Grand Forks, ND, Sept 2017.

In Subtask 6.2, the merits of two CO_2 capture strategy concepts were investigated. Industries and utilities continue to look for ways to decrease their carbon footprint as concerns mount about the potential role of CO_2 in climate change. These methods include improving process efficiencies so that less carbon-based fuel is used, switching to fuels with lower fossil carbon content (e.g., biomass or biomass blends, augmentation by wind or solar power), and capturing the CO_2 produced for either beneficial use or permanent storage. Capture and storage of the CO_2 can enable existing industrial and power generation facilities to meet the current national CO_2 reduction goals.

This approach is being demonstrated at large scale in several tests around the world and at commercial scale at the SaskPower Boundary Dam power station in Saskatchewan, Canada, and the Petra Nova project at the WA Parish generating station southwest of Houston, Texas. Unfortunately, the capture portion of the approach is currently expensive, and additional research is needed to find ways to decrease the cost. Reducing the cost of CO_2 capture will require that new technologies be developed across the various platforms (precombustion, postcombustion, oxyfuel combustion), the efficiency and effectiveness of existing technologies be improved, and pretreatment technologies that can improve the performance of a capture technology continue to be developed and optimized.

The EERC has developed two CO_2 capture concepts that merit preliminary experimental evaluation to determine if additional testing is warranted. These concepts form the basis of the work conducted under this subtask in two activities.

The first activity was a ministudy to determine if the addition to an amine CO_2 capture solvent of a condensable liquid with a boiling point lower than that of water would increase the stripping efficiency in the regeneration step. The concept is that the low-boiling-point liquid acts as a sweep gas during solvent regeneration, increasing the CO_2-stripping efficiency, which in turn enables the amine solvent to have a greater working capacity and/or a lower regeneration temperature. Cooling of the gas stream exiting the regeneration vessel would separate the

condensable sweep gas from the CO_2 so that the condensed liquid could be combined with the CO_2-rich amine.

Twelve candidate condensable sweep gas compounds were identified, which were reduced to two compounds for experimental testing: n-pentane and cyclohexane. The other candidate compounds were rejected because of cost or safety or because the boiling point was not significantly lower than water.

Small laboratory bench experiments were conducted with the two sweep gas compounds by measuring the carbon concentration of the prepared solvent mixtures (amine + sweep gas compound in a 9/1 volumetric ratio) before and after distillation. Carbon concentration was determined using total inorganic carbon and gas chromatograph analyses. Comparison of the analytical results for the sweep gas samples and the baseline, i.e., CO_2-loaded MEA with no additive, showed the impact of the added components. Experimental results show that a combination of MEA with either n-pentane or cyclohexane does not measurably change the MEA regeneration energy requirement. The starting and ending CO_2-loading levels for the test cases were not significantly different than that of the baseline case. No benefit was measured although these compounds theoretically indicated a benefit to the process.

The second activity was a ministudy focused on carbon-based materials, including biomass and coal-derived ACs, for CO_2 sorbents. The classical pressure swing and thermal swing adsorption (PSA and TSA) and desorption processes used in gas separation are both energy-intensive and time-consuming. The sorbent bed configuration and the process operation (particularly desorption) are the factors that play a major role in the gas desorption, which is a rate-determining process, while the sorbent composition provides preferential gas separation. An alternative to PSA and TSA processes can be designed by controlling these characteristic features of the sorbent bed and its operation.

The goal of the experimental work conducted on this concept is to conduct a preliminary evaluation of the sorbent bed configuration and process operation and use low- or zero-cost coal-based sorbent as opposed to specially engineered sorbents. The objective is to develop a comparative understanding of alternative bed configurations to understand the effect of a change in gas path length on the desorption process.

Four carbon sorbents were selected to be characterized and evaluated in a small laboratory bench apparatus. The carbon was prepared in the form of a packed bed, which was introduced to a multicomponent gas mixture. The adsorption process was conducted and measured, followed by desorption.

The ministudy demonstrated the use of low- or zero-cost carbon-based sorbent material and aided the understanding of the importance and potential of improving the bed configuration and operation in developing an alternative to the energy- and time-intensive PSA and TSA processes. Although the scale and sophistication of the test apparatus do not represent the features of the already-conceived process, the ministudy supported learning of its potential to significantly improve the state-of-the-art sorbent-based capture technologies for precombustion CO_2 capture. Future efforts will be targeted at understanding performance of the technology at subscale

in an actual process. The capture system will implement a more efficient operation that will significantly improve desorbed gas volume, reduce desorption time, and purge gas volume without requiring the typical PSA/TSA functions.

Task 7.0 – Project Management

Subtask 7.1 – Management and Reporting

Program Area:	CRD, CRDP, CS, and CC
Period of Performance:	7/1/08–5/31/18
Funding:	DOE: $801,900; Nonfederal: NA; Total: $801,900
EERC Subtask Manager:	Lucia Romuld
DOE Technical Monitor:	I. Andrew Aurelio
Nonfederal Partners:	NA
Final Report:	NA

Subtask 7.1 comprises the overall EERC management and reporting components of the DOE–EERC Joint Program on Research and Development for Fossil Energy-Related Resources (Cooperative Agreement No. DE-FC26-08NT43291). Pivotal to the success of any undertaking of this magnitude are the leadership abilities and management experience of the organizations' senior leadership and subtask managers and technical monitors for the individual subtasks.

The EERC Subtask 7.1 manager worked with the DOE Program Manager, EERC subtask managers, and DOE technical monitors to ensure the successful completion of all projects on time and on budget, that all contractual reporting requirements were met, and that the findings of this important research were communicated through technical presentations, peer-reviewed publications, and other outreach opportunities. In all, 75 projects were undertaken and successfully completed over the course of the 10-year program.