DOE–EERC JOINTLY SPONSORED RESEARCH PROGRAM

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Federal Energy Technology Center
U.S. Department of Energy
PO Box 10940, MS 921-143
Pittsburgh, PA 15236-0940

Performance Monitor: Mildred Perry

Prepared by:

John G. Hendrikson
Everett A. Sondreal

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

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LIST OF ABBREVIATIONS AND ACRONYMS

AA	atomic absorption
ACAA	American Coal Ash Association
ADE	Alaska Division of Energy
AEFGC	atmospheric entrained-flow gasification and combustion (simulator)
AGR	acid gas removal
AIDEA	Alaska Industrial Development and Export Authority
APF	advanced particle filter
ASTM	American Society for Testing and Materials
bbl	barrel
BHGFV	bench-scale hot-gas filter vessel
BTEX	benzene, toluene, ethylbenzene, and xylene
B&W	Babcock & Wilcox
CAAA	Clean Air Act Amendments
CABRE	Coal Ash Behavior in Reducing Environments
CaO	lime, calcium oxide
CAPD	Coal Ash Properties Database
CAPP	Canadian Association of Petroleum Producers
CARRC	Coal Ash Resources Research Consortium
CCB	coal combustion byproduct
CCP	coal combustion product
CCSEM	computer-controlled scanning electron microscopy
CE	capillary electrophoresis
CEA	Community Energy Alternatives
CEM	continuous emissions monitor
CEPS	conversion and environmental process simulator

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

CFBC	circulating fluidized-bed combustor
CFBR	continuous fluid-bed reactor
CFR	Code of Federal Regulations
COHPAC	compact hybrid particulate collector
CQE	Coal Quality Expert
CRIP	controlled retracting injection point
CTF	combustion test facility
CTI	critical thickness index
CWF	coal–water fuel
DEA	diethanolamine
DGC	Dakota Gasification Company
DMR	Department of Mineral Resources (Thailand)
DMT	dimethyl terephthalate
DOE	U.S. Department of Energy
dscm	dry standard cubic meter
DTA	differential thermal analysis
DTF	drop-tube furnace
EC	electrical conductivity
ECN	Netherlands Energy Research Foundation
EEI	EnerTech Environmental, Inc.
EERC	Energy & Environmental Research Center
EESI	Environmental Energy Systems, Inc.
EG	ethylene glycol
ELW	extended linked well
EPA	U.S. Environmental Protection Agency

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
ETI	Environmental Technologies International
FACT	Facility for the Analysis of Chemical Thermodynamics
FBC	fluid- or fluidized-bed combustion
FEGT	furnace exit gas temperature
FETC	Federal Energy Technology Center
FGD	flue gas desulfurization
FP&L	Florida Power & Light Company
FTE	Freeze–Thaw/Evaporation®
FT-IR	Fourier transform infrared
GC	gas chromatography
GC–AED	gas chromatography–atomic emission detection
GC–FID	gas chromatography–flame ionization detection
GC–MS	gas chromatography–mass spectrometry
GRI	Gas Research Institute
HAP	hazardous air pollutant
HDPE	high-density polyethylene
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
$HgCl_2$	mercuric chloride
HHV	higher heating value
HNO_3	nitric acid
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

HTTT	high-temperature tensile tester
HWD	hot-water drying
IAC	iodine-impregnated carbon
IC	ion chromatography
ICAP	inductively coupled argon plasma spectroscopy
ICCI	Illinois Clean Coal Institute
ICR	Information Collection Request
IESP	infrared emission sampling probe
IF&P	Industrial Filter & Pump
IGCC	integrated gasification combined cycle
IR	infrared
JSRP	Jointly Sponsored Research Program
KCl	potassium chloride
$KMnO_4$	potassium permanganate
KRCMC	Knife River Coal Mining Company
LAC	lignite-based activated carbon
LLQ	lower limit of quantitation
LOI	loss on ignition
LRC	low-rank coal
LRCWF	low-rank coal–water fuel
LTL	long-term leaching
LTOP	low-temperature oxygen plasma
maf	moisture- and ash-free
MCL	maximum concentration limits
MDEA	methyldiethanolamine

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

MDU	Montana–Dakota Utilities
MEA	monoethanolamine
MESA	Mercury Speciation Adsorption (method)
mf	moisture-free
MGP	manufactured gas plant
MMBtu	million British thermal units
MMT	mineral matter transformation
MRS	Mercury Recovery Services, Inc.
NH_3-N	ammonia nitrogen
NO_x-N	nitrogen oxides
NSPS	New Source Performance Standards
ODTF	optical drop-tube furnace
OPC	ordinary portland cement
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PCP	postconsumer plastics
PDU	process development unit
PEL	permissible exposure limit
PEFG	pressurized entrained-flow gasifier
PET	polyethylene terephthalate
PFBC	pressurized fluidized-bed combustion
PFBR	pressurized fluidized-bed reactor
PIANO	paraffins, isoparaffins, aromatics, naphthenes, and olefins
PP	polypropylene
ppb	parts per billion

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

ppm	parts per million
PRB	Powder River Basin
PSCD	particle-size and composition distribution
psi	pounds per square inch
PTC	particulate test combustor
PTFE	polytetrafluoroethylene
PTGA	pressurized thermogravimetric analyzer
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RDF	refuse-derived fuel
RFO	residual fuel oil
RM1	Rocky Mountain 1
RSD	relative standard deviation
RTC	Resource Technology Corporation
RVP	Reid vapor pressure
SEM	scanning electron microscope
SEMPC	scanning electron microscope point count
SFE	supercritical fluid extraction
SGLP	synthetic groundwater leaching procedure
SNCR	selective noncatalytic reduction
SO_2, SO_3	sulfur dioxide, sulfur trioxide
SPME	solid-phase microextraction
TA	terephthalic acid
TCLP	toxicity characteristic leaching procedure

Continued . . .

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

TEG	triethylene glycol
TGA	thermogravimetric analysis
TKN	total Kjeldahl nitrogen
TON	total organic nitrogen
TPH	total petroleum hydrocarbons
TRDU	transport reactor development unit
UAF	University of Alaska–Fairbanks
UCG	underground coal gasification
YBP	years before present

DOE–EERC JOINTLY SPONSORED RESEARCH PROGRAM
COOPERATIVE AGREEMENT DE-FC21-93MC30098
FINAL REPORT

EXECUTIVE SUMMARY

U.S. Department of Energy (DOE) Cooperative Agreement DE-FC21-93MC30098 funded through the Office of Fossil Energy and administered at the Federal Energy Technology Center (FETC) supported the performance of a Jointly Sponsored Research Program (JSRP) at the Energy & Environmental Research Center (EERC) with a minimum 50% nonfederal cost share. The objective of the JSRP was to advance the deployment of advanced technologies for improving energy efficiency and environmental performance through jointly sponsored research on topics that would not be adequately addressed by the private sector alone. The selection of particular research projects was guided by a combination of DOE priorities and market needs, as provided by the requirement for joint venture funding approved both by DOE and the private sector sponsor. The JSRP is a complement to an associated Base Program, which seeks to further the understanding of basic scientific and engineering foundations for new and improved technologies. This JSRP Cooperative Agreement and the complementary Base Cooperative Agreement were designed as a model for research, development, demonstration, and commercialization partnerships between government, industry, and the applied science and engineering community that can bring cutting-edge science closer to commercial application.

Under this agreement covering the period from fiscal year 1993 through 1997, the EERC negotiated the 64 JSRP tasks shown in Table 1. The DOE share of these projects was $11,997,297 (43%), while the nonfederal share totaled $16,189,257 (57%). The nonfederal sponsors are listed on Table 2. The EERC's internal goal of 60% nonfederal funding was achieved in each of the last three fiscal years.

The JSRP tasks funded under this agreement covered a broad range of topics of mutual interest to both DOE's Office of Fossil Energy and nonfederal sponsors, ranging from fundamental research to highly applied development. The topics addressed included climate change; resource characterization; underground coal gasification; air toxic emissions; groundwater quality; environmental remediation of soils; fuel upgrading, blending, and switching; boiler performance indices addressing ash fouling and other operational issues; optimizing atmospheric fluid-bed combustion sulfur removal and reducing bed agglomeration; ash behavior under reducing conditions; hot-gas filter blinding; coal combustion byproduct utilization; alternative fuels and chemicals; plastics recycling; and distributed power generation.

EERC–DOE COOPERATIVE AGREEMENT
JOINTLY SPONSORED RESEARCH PROGRAM
FINAL REPORT

1.0 INTRODUCTION

U.S. Department of Energy (DOE) Cooperative Agreement DE-FC21-93MC30098 funded through the Office of Fossil Energy and administered at the Federal Energy Technology Center (FETC) supported the performance of a Jointly Sponsored Research Program (JSRP) at the Energy & Environmental Research Center (EERC) with a minimum 50% nonfederal cost share to assist industry in commercializing and effectively applying efficient, nonpolluting energy technologies that can compete effectively in meeting market demands for clean fuels, chemical feedstocks, and electricity in the 21st century. The JSRP is a vehicle for the deployment of advanced research concepts developed under an associated Base Program, which seeks to further the understanding of basic scientific and engineering foundations for new and improved technologies. This two-part Cooperative Agreement (Base and JSRP) is designed as a model for research, development, demonstration, and commercialization partnerships between government, industry, and the applied science and engineering community that can bring cutting-edge science closer to commercial application.

2.0 OVERALL OBJECTIVES

The objective of the JSRP was to advance the deployment of advanced technologies for improving energy efficiency and environmental performance through jointly sponsored research on topics that would not be adequately addressed by the private sector alone. Examples of such topics include the barriers to hot-gas cleaning impeding the deployment of high-efficiency power systems and the search for practical means for sequestering CO_2 generated by fossil fuel combustion. The selection of particular research projects was guided by a combination of DOE priorities and market needs, as provided by the requirement for joint venture funding approved both by DOE and the private sector sponsor. The research addressed many different energy resource and related environmental problems, with emphasis directed toward the EERC’s historic lead mission in low-rank coals (LRCs), which represent approximately half of the U.S. coal resources in the conterminous states, much larger potential resources in Alaska, and a major part of the energy base in the former U.S.S.R., East Central Europe, and the Pacific Rim. The Base and JSRP agreements were tailored to the growing awareness of critical environmental issues, including water supply and quality, air toxics (e.g., mercury), fine respirable particulate matter ($PM_{2.5}$), and the goal of zero net CO_2 emissions.

3.0 GENERAL PROJECT APPROACH

Projects funded under the Cooperative Agreement derived both from the maturation of research performed under the Base Program and from particular needs advanced by industry. The scope of the JSRP agreement provides flexibility to change research priorities to respond to DOE program priorities, funding levels, and market needs. In general, the research topics selected fit within the objectives of seven research areas: 1) resource characterization and waste management, 2) air quality assessment and control, 3) advanced power systems, 4) advanced fuel forms, 5) value-added coproducts, 6) advanced materials, and 7) strategic studies. Work plans for particular JSRP projects were arranged by the EERC in consultation with the private sector sponsor and forwarded to FETC for individual approval.

4.0 ACCOMPLISHMENTS

Under this agreement covering the period from fiscal year 1993 through 1997, the EERC negotiated the 64 JSRP tasks shown in Table 1 (p. 9). The DOE share of these projects was $11,997,297 (43%), while the nonfederal share totaled $16,189,257 (57%). The EERC's internal goal of 60% nonfederal funding was achieved in each of the last three fiscal years.

The JSRP tasks funded under this agreement covered a broad range of topics of mutual interest to both DOE's Office of Fossil Energy and nonfederal sponsors, ranging from fundamental research to highly applied development. The topics addressed included climate change; resource characterization; underground coal gasification; air toxic emissions; groundwater quality; environmental remediation of soils; fuel upgrading, blending, and switching; boiler performance indices addressing ash fouling and other operational issues; optimizing atmospheric fluid-bed combustion sulfur removal and reducing bed agglomeration; ash behavior under reducing conditions; hot-gas filter blinding; coal combustion byproduct utilization; alternative fuels and chemicals; plastics recycling; and distributed power generation. Table 2 (p. 13) lists the nonfederal sponsors for each task.

Highlights

Climate Change

A task on climate change cofunded by EPRI studied erosion and deposition cycles that can be deduced from the alluvial record in badlands terrain in western North Dakota for paleosol interpretation of value to climate modeling. One setting, the Douglas Creek Locality, offered sufficient chronometric and configurational data to interpret numerous soil-forming conditions in a short tributary of the Missouri River from 5240 to 2585 years (plus or minus the analytical error) before present. Stable landform conditions were shown to be periodically interrupted 15 times by alluvial sedimentation occurring when soil-forming processes ceased. On the basis of radiocarbon dates, the cessation occurred with some regularity at an average period of 177 years, which reflected a change in climate, specifically precipitation, from wetter times of soil forming to drier times of increased erosion and sedimentation. Future research will seek to understand the climate-forming factors that might establish such long-term atmospheric patterns and to use such cyclicity information to interpret global climate models in light of natural climate change deduced from the geological record.

Air Toxics Control

Four tasks on measurement and control of air toxic metal emissions from coal combustion were performed cofunded by EPRI, the North Dakota Lignite Research Council, four electric utilities, and an engineering company. These JSRP tasks were a complement to work performed under the Base Agreement that evaluated DOE data on air toxic emissions from eight coal-burning power plants to assess regulatory requirements under the 1990 Clean Air Act Amendments (CAAA).

Most of the toxic trace elements studied were retained in the fly ash and collected in an electrostatic precipitator or baghouse, including antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, and nickel. Mercury and selenium were emitted to various degrees in the stack gas. Studies to characterize volatile trace metal emissions were focused on speciated forms of mercury, either elemental mercury (Hg^0) or the oxidized form (Hg^{2+}).

A comparative evaluation of sampling methods indicated that some methods, including U.S. Environmental Protection Agency (EPA) Method 29, overestimate the oxidized form of mercury to varying degrees depending on the level of acid gases present. However, modifications of EPA Method 29 represented by the Ontario Hydro and tris-buffer methods speciated mercury correctly on the basis of known spiked concentrations.

The capture of mercury from combustion gases on various active carbon sorbents was shown to depend on temperature and the dissimilar mercury forms that result from burning different test coals. Above 250°F, only the oxidized form was effectively captured. In a complementary task under the Base Program, the EERC developed and patented carbon and metal oxide sorbents that serve to catalyze the oxidation of Hg^0 to Hg^{2+}, which can be effectively captured at temperatures up to about 650°F. In another JSRP task, activated chars produced by hydrothermal processing of lignite were tested for mercury sorption, with subsequent reactivation of the char and recovery of mercury by further hydrothermal treatment.

Water Quality and Soil Remediation

Eight JSRP tasks have addressed soil and groundwater contamination at energy production sites, specifically including natural gas production and processing facilities. Cofunding has been provided by groups that include the American Petroleum Institute, Gas Research Institute (GRI), EPRI, the Canadian Association of Petroleum Producers, the National Energy Board of Canada, and a number of oil and gas companies, environmental remediation companies, and instrument companies.

Rapid and economical methods were developed for extracting and analyzing for petroleum hydrocarbons in soil matrices based on supercritical fluid extraction coupled with gas chromatography and infrared spectrometry. Several field-transportable analytical techniques were validated for accuracy and precision for quantitation of mercury in soils.

A comprehensive evaluation of soil and groundwater contamination at natural gas industry sites identified mercury, glycols, and the amines used for removing acid gases from natural gas and their thermal reaction products as subsurface contaminants of major concern. Site characterization data have been obtained, and cleanup options have been tested.

A focused research effort has been directed toward evaluating the transport, fate and remediation of the most commonly used amines, diethanolamine (DEA), methyldiethanolamine (MDEA), and monoethanolamine (MEA). Transport study results indicate that high-concentration spills of amines initially undergo significant transport in the subsurface, but that transport is attenuated by the buffering effect of the soil on pH as the plume spreads and is diluted. A significant portion of the amine-related contamination is recalcitrant to biodegradation. Landfarming was demonstrated to successfully remove much of the contamination, but considerable toxicity remained, as indicated by plant response and earthworm survival results.

Ex situ biological treatment in a two-stage rotating biological contactor effectively removed hydrocarbons and ammonia from contaminated groundwater being directed through a pump-and-treat system at a gas plant.

A novel freeze–thaw/evaporation (FTE®) process was demonstrated under the JSRP for natural freeze crystallization of wastewater from oil and gas operations to produce reusable-quality purified water and a concentrated liquid waste stream. The technology has the potential for broad application in economically treating large volumes of contaminated water, including the treatment of brackish waters as a source of potable or industrial water. Related work has been performed on the design of cost-effective and environmentally safe evaporation and holding ponds.

Fuel Upgrading and Blending

Seven JSRP tasks devoted to upgrading and testing individual coals or coal blends to meet sulfur compliance, moisture reduction, stability criteria, or other requirements were cofunded by groups that included EPRI, three coal companies, two utilities, two process developers, and agencies in Illinois, North Dakota, Alaska, and Thailand.

In reference to sulfur removal, combustion tests on an Illinois Basin coal and two coal–char blends with reduced sulfur levels showed that a blend prepared from high-temperature char with addition of hydrated lime caused severe slagging and fouling, while a second blend prepared from low-temperature char without lime exhibited no increase in slagging and fouling in relation to the original coal. Promising levels of organic sulfur removal were achieved in bench-scale batch tests on Illinois Basin coal by extraction with hot subcritical water, reducing total sulfur from 3.0 to 0.7 wt%, but lesser removals were observed in scaleup tests in a 100-lb/hr continuous process. Test results on the blending of low-sulfur Powder River Basin subbituminous coals with bituminous coals for sulfur compliance generally showed favorable improvement in flame stability and carbon burnout, but also some unfavorable derating of pulverizer capacity and increased low-temperature ash fouling.

In upgrading LRCs, tests on North Dakota lignite involving various combinations of gravity cleaning, ion exchange in carbonic acid, high-gradient magnetic separation, and agglomeration in a polar oil produced low-moisture briquettes with a heating value near 10,000 Btu/lb, sulfur emissions reduced from 2.0 to 0.9 lb SO_2/MMBtu, and a reduced sodium content. Tests on hot-roll briquetting of K-Fuel® product without binder produced relatively strong briquettes at a suitably selected process temperature, which served to enhance stability toward water reabsorption, friability, and spontaneous heating for applications in utility boilers, industrial stokers, and domestic heating furnaces. Slurry fuels with from 50% to over 60% dry solids content were prepared by hydrothermal processing of high-moisture Alaska subbituminous coal, North Dakota and Thai lignites, and a variety of low-sulfur waste materials, including municipal solid waste, municipal sludge, and pulp and paper sludge, and the products were selectively tested in EERC combustion and gasification facilities.

Improving Boiler Efficiency and Availability

Seven JSRP tasks devoted to improving boiler operation by accommodating boilers to coal quality parameters were cofunded by groups that included EPRI, ten utilities, a boiler manufacturer, an engineering company, and the North Dakota Industrial Commission.

Coal quality indices were developed and perfected for assessing fireside fouling and slagging and other performance factors, including coal grindability, slag-tapping, tube erosion, sootblower effectiveness, and stack opacity. Indices were subsequently validated against field data on a range of coals burned at several utilities. Computer codes providing integrated versions of indices for use on personal computers were compiled, including Coal Quality Expert (CQE), developed in cooperation with Black and Veatch, and a simpler, more adaptable version designated PCQUEST, which was developed in-house at the EERC.

Coal-blending strategies for minimizing ash fouling and slagging were devised on the basis of detailed lignite resource characterization. These were incorporated into a computer program for mine planning. A zirconium additive was evaluated for mitigation of ash deposition occurring during combustion of residual fuel oil.

An infrared emission sampling probe (IESP) was designed as an accessory to a Fourier transform infrared (FT-IR) spectrometer to monitor deposit growth, with potential for adaptation to determine deposit chemistry by in situ measurements.

Seven short courses providing practical technology transfer based on recent advances in research on ash deposition were presented to groups of utility boiler operators in Florida, Illinois, North Dakota, Minnesota, Wisconsin, and the Netherlands.

Ash and Sorbent Behavior in Advanced Power Systems

Six JSRP tasks have focused on ash- and sorbent-related problems in advanced power systems.

Tasks in the Coal Ash Behavior in Reducing Environments (CABRE I and II) projects have been cofunded by EPRI and the major U.S. and European gasifier developers. Current work on CABRE II is being conducted in collaboration with the Netherlands Energy Research Foundation (ECN) with the objectives of understanding the effects of vapor species and fine particulates on deposit formation in entrained-flow gasifiers and the related mechanisms of deposit sintering and strength development, and of developing predictive indices and mitigation methods. Progress in this ongoing research was in areas that included shakedown of a pressurized entrained-flow gasifier (PEFG) simulator, identification of impacts of fuel gas composition on slag viscosity, and prediction of vapor species and fine particulate compositions by the Facility for the Analysis of Chemical Thermodynamics (FACT) code.

An ongoing task on hot-gas filter ash characterization, cofunded by a consortium that includes EPRI and eight U.S. and overseas technology vendors, is directed toward understanding the mechanisms that cause ash blinding and bridging on hot-gas particulate filters and devising remedies. Samples of coal, bed material, and/or filter ash have been obtained for analysis and assessment from the American Electric Power Tidd PFBC (pressurized fluidized-bed combustion) plant and from seven centers operating developmental PFBC or IGCC (integrated gasification combined-cycle) facilities. Hot-gas filter tests are being run in the EERC's pilot-scale transport reactor development unit (TRDU), which models the Kellogg gasifier at the DOE facility in Wilsonville, Alabama. Tests are also being conducted in a bench-scale PFBC to determine factors affecting the size and composition of filter ash particles. Thermochemical equilibrium modeling based on the FACT code has been used to identify the liquid phases responsible for sintering in particular ash deposits, including those from the Tidd plant. A training presentation package based on detailed photos, samples, and operating data from a 200-hour filter test on the TRDU was prepared and distributed to other test centers and filter manufacturers.

Three tasks were performed for groupings of power companies and state agencies addressing optimization of bed performance in FBCs (fluidized-bed combustors). Methods were developed to predict deposition and agglomeration in FBCs based on chemical and physical measurements on deposited materials and adaptation of models designed to predict low-temperature sulfate-bonded deposition in pulverized coal-fired boilers. Bed materials, sorbents, and additives were identified that greatly reduced bed agglomerating tendencies. Tests are in progress on high-sulfur lignite containing variable amounts of sodium to optimize bed material, excess air, and bed temperature for achieving both high SO_2 capture and high boiler load carrying capacity without incurring severe agglomeration. Tests on the regeneration and pelletization of spent limestone sorbent from the EERC pilot-scale PFBC were successful in recovering a concentrated stream of SO_2 and recycling limestone to reduce sorbent usage and waste disposal by 84.5% when the unit was operating on high-sulfur fuel.

Utilization of Coal Combustion Byproducts

Three tasks devoted to the use of coal combustion byproducts were cofunded by groups that included the American Coal Ash Association, the North Dakota Industrial Commission, four power companies, and two recycling companies. Work is coordinated through the EERC's Coal Ash Resources Research Consortium (CARRC). Research for advancing utilization applications was performed on the use of fly ash in high-ash concrete, controlled low-strength fill, and formulated cements, addressing both engineering properties and environmental leaching criteria. A computer database containing analytical and engineering information on combustion byproducts was prepared for the American Coal Ash Association and DOE. Pilot-scale tests were performed on the oxidation of scrubber sludge to produce wallboard-quality gypsum. Educational efforts to increase utilization were directed to CARRC members and to the coal combustion byproduct industry at large.

Alternative Liquid Fuels and Chemicals

Four tasks on liquid fuels and chemicals were cofunded by the National Corn Growers Association, the Dakota Gasification Company, the American Plastics Council, and the 3M Company.

Work under the EERC's National Alternative Fuels Laboratory on the use of ethanol as a gasoline additive indicated that problems with high Reid vapor pressure (RVP) reported for 10% ethanol blends are partly attributable to denaturant and water effects, opening opportunities to reduce RVP for these blends.

Work on the purification of phenol from the Dakota Gasification Company plant showed that an alumina catalyst could be used to destroy certain reactive impurities, but at the expense of producing unacceptable amounts of higher-molecular-weight polymers.

Fluidized-bed pyrolysis methods were developed and scaled up to 100 lb of feed/hr for producing olefins and halogen-free liquid monomers from mixed-plastic wastes that included difficult-to-recycle materials such as polyvinyl chloride (PVC) and polyethylene terephthalate (PET). Temperature and residence time were optimized to maximize yields of either light olefins or organic liquids, depending on the analysis of the feed stream. The chlorine content of liquid products was reduced to 20 ppm starting with a feed stream containing 2% to 5% PVC.

U.S. Power Technologies for Remote-Site and Overseas Applications

Two tasks sited in Alaska and Thailand were performed with the advancement of U.S. technology exports as a primary objective. The first task concerned the development of remote-site power generation opportunities for Alaska, with the added incentive of transferring distributed power generation technologies to other indigenous communities in the United States and in developing countries. An Alternative Power Generation Workshop was held in Anchorage, Alaska, in 1994 to obtain input on user requirements and technology options from state agencies, technology suppliers, and end users in Alaska. A second workshop in Seattle, Washington, in

1995 explored specific project opportunities for commercializing technologies that would use indigenous natural gas, coalbed methane, coal, biomass, or municipal solid waste. The EERC, under JSRP and related DOE funding, has assisted Alaskan power companies and state agencies in performing engineering studies on small FBC and fuel cell systems as alternatives to diesel electric systems, with a decision pending on project commitment and detailed design. A market survey was conducted to assess opportunities for worldwide marketing of distributed power systems to developing countries.

An evaluation of underground coal gasification (UCG) was performed for a project at the Saba Yoi coalfield in southern Thailand to supply syngas for petrochemical production and electric power generation. The task reviewed available geological and hydrogeological data and project requirements and developed a preliminary economic evaluation.

5.0 DETAILED TASK DESCRIPTIONS

Descriptions for each of the tasks follow Table 2.

Table 1
U.S. Department of Energy
Cooperative Agreement DE-FC21-93MC30098
Jointly Sponsored Research Program

Task No.	Task Title	DOE Share, $	Participant Share, $	Total, $
1	Multiple-Use Marketing of Lignite	20,000	20,000	40,000
2	Seventeenth Biennial Low-Rank Fuels Symposium	35,000	35,000	70,000
3	Slagging and Fouling Assessment of a Coal and Coal Chars	15,175	15,175	30,350
4	Processing Concerns in Thermal Recycling of Waste Materials	131,101	131,113	262,214
5	Sorbent Regeneration from Circulating Fluidized-Bed Combustors	44,956	44,966	89,922
6	Evaluation/Interpretations of Rocky Mountain 1 Data	76,950	79,269	156,219
7	Agglomeration and Deposition in FBCs	440,000	440,000	880,000
8	Development of a Fireside Performance Index: Convective Pass Fouling and Fly Ash Collectability	370,000	370,000	740,000
9	(CANCELED) Transport Reactor Demonstration Unit Construction	0	0	0
10	Timing of the Deposition of Uppermost Cretaceous and Paleocene Coal-Bearing Deposits in the Greater Glendive Area, Montana and North Dakota	33,980	33,980	67,960
11	Coal Agglomeration Consortium (see Table 2)	100,000	100,000	200,000
12	(CANCELED) Formulation and Evaluation of Controlled Low-Strength Materials Utilizing Byproducts from Montana–Dakota Utilities	0	0	0
13	Phenol Purification Studies	22,000	22,000	44,000
14	Effect of Ethanol Denaturant on Gasoline RVP	49,978	49,981	99,959
15	Process Development Unit Test Program for Thermally Recycled Plastics	630,000	809,120	1,439,120
16	Bench-Scale Preparation and Combustion of RDF/Coal Slurry Fuels	95,000	135,000	230,000

Continued . . .

Table 1 (continued)

Task No.	Task Title	DOE Share, $	Participant Share, $	Total, $
17	Enhanced Air Toxics Control	712,047	767,403	1,479,450
18	Coal Ash Resources Research Consortium	310,240	437,294	747,534
19	The Application of FBC Residues for High-Volume Utilization Options (see Table 2)	160,000	160,000	320,000
20	FT-IR Spectroscopic Investigation of Fireside Deposit in a Pilot Plant Combustor	45,000	45,000	90,000
21	Sour Gas Plant Remediation Technology Research and Demonstration Project	380,250	502,250	882,500
22	Evaluation of Supercritical Fluid Extraction (SFE) for Analysis of Petroleum Industry Wastes	100,000	100,000	200,000
23	Gas Industry Groundwater Research Program	1,699,754	1,700,000	3,399,754
24	Pilot Plant Assessment of Blend Properties	15,881	195,000	210,881
25	Physical Cleaning of Lignite	30,000	30,000	60,000
26	Remote Site Power Generation Opportunities for Alaska	250,000	271,400	521,400
27	Alaskan Low-Rank Coal–Water Fuel Environmental Attributes and Combustion Test Marketing	50,000	62,000	112,000
28	An Assessment of the Subsurface Fate of Monoethanolamine at Sour Gas-Processing Plant Sites	165,130	247,032	412,162
29	Mitigation of Air Toxics from Lignite Generation Facilities	100,000	100,000	200,000
30	Hot-Gas Filter Ash Characterization Project	825,000	1,005,000	1,830,000
31	Formal Evaluation of Flue Gas Chemical Measurement Methods Phase I – Verification of Mercury Speciation by EPA (Draft) Method 29	1,262,355	1,996,992	3,259,347
32	Organic Sulfur Removal from Coal with Super and Subcritical Water	227,218	298,527	525,745
33	Upgraded North Dakota Lignite – Production of Test Quantities	25,000	40,000	65,000

Continued . . .

35	Evaluation of Field Analytical Techniques for Mercury in Soil	40,000	89,500	129,500

Table 1 (continued)

Task No.	Task Title	DOE Share, $	Participant Share, $	Total, $
36	Combustion Characterization of Carbonized RDF from Temperature Optimization Tests	200,000	304,096	504,096
37	Recent Advances in Research on Ash Deposition in Utility Boilers	60,331	90,502	150,833
38	Witnessing, Sampling, and Validating Mercury Remediation Technology Research and Demonstrations	40,000	60,500	100,500
39	Preparation and Gasification of Thailand Coal–Water Fuels	49,771	75,000	124,771
40	Mercury Sorbent Evaluation	124,350	185,650	310,000
41	Lignite Resource Characterization Evaluation for Mitigation of Ash Disposition	152,000	228,000	380,000
42	Holocene Cyclicity in Western North Dakota – Climate Change Interpreted from Fluctuations in Alluvial Sedimentation	64,972	99,964	164,936
43	Oxidation of North Dakota Scrubber Sludge for Soil Amendment and Production of Gypsum	40,000	80,000	120,000
44	Pilot Plant Assessment of Fly Ash Agglomeration	209,993	318,007	528,000
45	Small-Scale Demonstration of the Freeze–Thaw Evaporation Process to Treat Oil and Gas Produced Waters	741,530	1,291,530	2,033,060
46	Training and Support for Hot-Gas Filter Testing	20,539	20,539	41,078
47	Development of a Coal Combustion Byproducts (CCBs) Database System	19,800	29,700	49,500
48	Coal Ash Behavior in Reducing Environments (CABRE) II	300,700	599,300	900,000
49	Validation of Fireside Performance Indices	240,000	360,000	600,000
50	Deposition of Lignites in the Fort Union Group and Related Strata of the Northern Great Plains	25,000	25,000	50,000

Continued . . .

51	Oxygen Plasma Unit for Soil Decontamination: Demonstration of a Field-Scale Unit	199,703	499,000	698,703

Table 1 (continued)

Task No.	Task Title	DOE Share, $	Participant Share, $	Total, $
52	Evaluation of a Zirconium Additive for the Mitigation of Molten Ash Formation During Combustion of Residual Fuel Oil	25,373	38,060	63,433
53	Construction, Demonstration, and Evaluation of an Economic and Environmentally Safe Evaporation and Holding Pond Design	70,000	160,000	230,000
54	Activated Carbon for Environmental Applications	26,668	40,000	66,668
55	Binderless Agglomeration of K-Fuel® Product Preliminary Evaluation	175,601	261,288	436,889
56	Preliminary Economic Evaluation of UCG at Saba Yoi, Thailand	60,000	90,000	150,000
57	Preparation and Combustion of Coal–Water Fuel from a Lignite from Southern Thailand	27,490	41,240	68,730
58	Optimizing Performance of the Heskett Station	73,000	110,000	183,000
59	Binder Modification and Development for Briquetting Steel Mill Residues	54,361	81,529	135,890
60	Characterizing Soil/Water Sorption and Desorption Behavior of BTEX and PAHs Using SFE	75,000	75,000	150,000
61	Characterization of a Fluidized-Bed Combustion Ash to Determine Potential for Environmental Impact	62,720	93,590	156,310
62	Reducing Power Production Costs by Utilizing Petroleum Coke	36,000	54,000	90,000
63	Characterization and Modeling of the Forms of Mercury from Coal-Fired Utility Power Plants	137,380	274,760	412,140
64	Mercury Formation and Fate	183,000	210,000	393,000
	Totals	**$11,997,297**	**$16,189,257**	**$28,186,554**

Table 2
Summary of Nonfederal JSRP Sponsors

Task No.	Task Title	Sponsor(s)
1	Multiple-Use Marketing of Lignite	Knife River Coal Mining Company, J.R. Simplot Company, and the North Dakota Industrial Commission
2	Seventeenth Biennial Low-Rank Fuels Symposium	American Coal Ash Association, BNI Coal, Ltd., Knife River Coal Mining Company, MDU Resources Group, Inc., Minnkota Power Cooperative, Minnesota Power, Northern States Power Company, N-R-G Energy, Inc., North American Coal Corporation, Otter Tail Power Company, and Utility Fuels, Inc.
3	Slagging and Fouling Assessment of a Coal and Coal Chars	Illinois State Geological Survey
4	Processing Concerns in Thermal Recycling of Waste Materials	American Plastics Council and the 3M Company
5	Sorbent Regeneration from Circulating Fluidized-Bed Combustors	Community Energy Alternatives (CEA)
6	Evaluation/Interpretations of Rocky Mountain 1 Data	Gas Research Institute (GRI)
7	Agglomeration and Deposition in FBCs	Foster Wheeler Development Corporation, Industrial Commission of North Dakota, Northern States Power, Riley Stoker, and EPRI
8	Development of a Fireside Performance Index: Convective Pass Fouling and Fly Ash Collectability	Union Electric, Northern States Power Company, Minnesota Power, EPRI, and Kansas City Power & Light
9	Transport Reactor Demonstration Unit Construction	CANCELED
10	Timing of the Deposition of Uppermost Cretaceous and Paleocene Coal-Bearing Deposits in the Greater Glendive Area, Montana, and North Dakota	National Geographic Society and State University of New York at Stony Brook
11	Coal Agglomeration Consortium	The sponsor decided not to pursue this project, and designated funds were not used.

Continued . . .

Table 2 (continued)

Task No.	Task Title	Sponsor(s)
12	Formulation and Evaluation of Controlled Low-Strength Materials Utilizing Byproducts from Montana–Dakota Utilities	CANCELED
13	Phenol Purification Studies	Dakota Gasification Company (DGC)
14	Effect of Ethanol Denaturant on Gasoline RVP	National Corn Growers Association
15	Process Development Unit Test Program for Thermally Recycled Plastics	American Plastics Council
16	Bench-Scale Preparation and Combustion of RDF/Coal Slurry Fuels	EnerTech Environmental, Inc. (EEI)
17	Enhanced Air Toxics Control	EPRI
18	Coal Ash Resources Research Consortium	Cooperative Power, National Minerals Corporation, Otter Tail Power Company, Portland Cement Association, Nebraska Ash, Northern States Power Company, Environmental Resource Corporation, Edison Electric Institute, and North Dakota Industrial Commission
19	The Application of FBC Residues for High-Volume Utilization Options	The sponsor decided not to pursue this project, and designated funds were not used.
20	FT-IR Spectroscopic Investigation of Fireside Deposit in a Pilot Plant Combustor	EPRI
21	Sour Gas Plant Remediation Technology Research and Demonstration Project	Canadian Association of Petroleum Producers (CAPP)
22	Evaluation of Supercritical Fluid Extraction (SFE) for Analysis of Petroleum Industry Wastes	American Petroleum Institute
23	Gas Industry Groundwater Research Program	GRI
24	Pilot Plant Assessment of Blend Properties	EPRI, Empire State Electric Energy Research Corporation, CONSOL, Inc., and Ziegler Coal
25	Physical Cleaning of Lignite	North Dakota Industrial Commission and Knife River Coal Mining Company

Continued . . .

Table 2 (continued)

Task No.	Task Title	Sponsor(s)
26	Remote Site Power Generation Opportunities for Alaska	Alaska Science & Technology Foundation, Usibelli Coal Mine, Inc., Placer Dome U.S., Inc., ENPAC Energy Pacific Corporation, Major International, Power Engineers, International Coal Preparation Consultants, Ltd., and University of Alaska–Fairbanks
27	Alaskan Low-Rank Coal–Water Fuel Environmental Attributes and Combustion Test Marketing	Alaska Division of Energy (ADE), International Coal Preparation Consultants, Ltd., and ENPAC Energy Pacific Corporation
28	An Assessment of the Subsurface Fate of Monoethanolamine at Sour Gas-Processing Plant Sites	CAPP, Canadian Occidental Petroleum, Ltd. (CanOxy), Environment Canada, and the National Energy Board of Canada
29	Mitigation of Air Toxics from Lignite Generation Facilities	EPRI, North Dakota Industrial Commission, Basin Electric Power Cooperative, Cooperative Power Association, Minnesota Power, and Montana–Dakota Utilities (MDU)
30	Hot-Gas Filter Ash Characterization Project	EPRI, Lurgi–Lentjes–Babcock (LLB), PowerGen, Schumacher America, Westinghouse, Electricité de France, the Netherlands Energy Research Foundation (ECN), ABB Carbon, and the Electric Power Development Company (EPDC)
31	Formal Evaluation of Flue Gas Chemical Measurement Methods Phase I – Verification of Mercury Speciation by EPA (Draft) Method 29	EPRI
32	Organic Sulfur Removal from Coal with Super and Subcritical Water	Illinois Clean Coal Institute (ICCI)
33	Upgraded North Dakota Lignite – Production of Test Quantities	North Dakota Industrial Commission, Knife River Coal Mining Company, and North American Coal Company
34	Coal Quality Expert Fouling and Slagging Algorithm Development	EPRI and Black & Veatch

Continued . . .

Table 2 (continued)

Task No.	Task Title	Sponsor(s)
35	Evaluation of Field Analytical Techniques for Mercury in Soil	GRI, General Electric, BioNebraska, Inc., Spectrace Instruments, and NOVA Corporation (Canada)
36	Combustion Characterization of Carbonized RDF from Temperature Optimization Tests	EEI
37	Recent Advances in Research on Ash Deposition in Utility Boilers	SaskPower, BHP Minerals, Arizona Public Services (APS), Wisconsin Power & Light, and individual conference participants
38	Witnessing, Sampling, and Validating Mercury Remediation Technology Research and Demonstrations	GRI, Cognis, Inc., Pittsburgh Mineral and Environmental Technologies, Inc., and Union Gas Company
39	Preparation and Gasification of Thailand Coal–Water Fuels	Thailand Department of Mineral Resources (DMR)
40	Mercury Sorbent Evaluation	EPRI
41	Lignite Resource Characterization Evaluation for Mitigation of Ash Disposition	Knife River Coal Mining Company and North Dakota Industrial Commission
42	Holocene Cyclicity in Western North Dakota – Climate Change Interpreted from Fluctuations in Alluvial Sedimentation	EPRI
43	Oxidation of North Dakota Scrubber Sludge for Soil Amendment and Production of Gypsum	Cooperative Power and the North Dakota Industrial Commission
44	Pilot Plant Assessment of Fly Ash Agglomeration	Thermal Energy Systems, Inc.
45	Small-Scale Demonstration of the Freeze–Thaw Evaporation Process to Treat Oil and Gas Produced Waters	Amoco Production Company, GRI, and RETEC
46	Training and Support for Hot-Gas Filter Testing	Industrial Filter & Pump (IF&P), 3M Company, and Pall Advanced Filters
47	Development of a Coal Combustion Byproducts (CCBs) Database System	American Coal Ash Association
48	Coal Ash Behavior in Reducing Environments (CABRE) II	ECN/Novem (Netherlands), KEMA Nederlands B.V., Elcogas (Spain), Krupp Koppers GmbH (Germany), Babcock–Hitachi, K.K. (Japan), and EPRI

Continued . . .

Table 2 (continued)

Task No.	Task Title	Sponsor(s)
49	Validation of Fireside Performance Indices	Mountain Inc., Foster Wheeler Development Corporation, Duke Power Company, Dairyland Power Cooperative, EPRI, D.B. Riley, Arkansas Power & Light, Wisconsin Power & Light, and Sauder Woodworking
50	Deposition of Lignites in the Fort Union Group and Related Strata of the Northern Great Plains	Philip M. McKenna Foundation
51	Oxygen Plasma Unit for Soil Decontamination: Demonstration of a Field-Scale Unit	AGSCO, Inc.
52	Evaluation of a Zirconium Additive for the Mitigation of Molten Ash Formation During Combustion of Residual Fuel Oil	Florida Power & Light Company (FP&L)
53	Construction, Demonstration, and Evaluation of an Economic and Environmentally Safe Evaporation and Holding Pond Design	EPRI
54	Activated Carbon for Environmental Applications	Environmental Energy Systems Incorporated (EESI)
55	Binderless Agglomeration of K-Fuel® Product Preliminary Evaluation	Kennecott Energy Corporation
56	Preliminary Economic Evaluation of UCG at Saba Yoi, Thailand	Thailand DMR
57	Preparation and Combustion of Coal–Water Fuel from a Lignite from Southern Thailand	Thailand DMR
58	Optimizing Performance of the Heskett Station	MDU and North Dakota Industrial Commission
59	Binder Modification and Development for Briquetting Steel Mill Residues	Heckett MultiServ
60	Characterizing Soil/Water Sorption and Desorption Behavior of BTEX and PAHs Using SFE	American Petroleum Institute and GRI
61	Characterization of a Fluidized-Bed Combustion Ash to Determine Potential for Environmental Impact	Malcolm Pirnie, Inc.
62	Reducing Power Production Costs by Utilizing Petroleum Coke	EPRI

Continued . . .

Table 2 (continued)

Task No.	Task Title	Sponsor(s)
63	Characterization and Modeling of the Forms of Mercury from Coal-Fired Utility Power Plants	EPRI
64	Mercury Formation and Fate	Minnkota Power Cooperative, Cooperative Power Association, North Dakota Industrial Commission, and EPRI

Task 1 – Multiple-Use Marketing of Lignite

The use of North Dakota lignite for spreader–stoker boilers is decreasing since lignite is slightly inferior to subbituminous coals. Lignite's delivered cost is similar to that of subbituminous coals, but lignite contains more sulfur and has more ash and sodium in the ash. The goal of this program, sponsored through the EERC–DOE JSRP and the Knife River Coal Mining Company, J.R. Simplot Company, and the North Dakota Industrial Commission, was to provide a market feasibility study for multiple uses of lignite in the city of Grand Forks, North Dakota. Lignite and sulfur-capturing additives were studied for their ability to clean agriculture wastewater and to determine if the lignite could be used after wastewater cleanup to generate steam and produce lignite briquettes, the objective being to determine if the second use would make lignite more economical overall.

Various combinations of lignite, waste slime sludges, lime (lime is a combustion sulfur-capturing agent), and an additive were used to produce clear, essentially odor-free water from potato wastewater. Collected residue containing starch material and lignite were successfully briquetted. A major cost in the upgrading of lignite (drying) is the capital and operating cost of dust-handling equipment. Preliminary tests indicate these costs may be reduced by proper pretreatment of the coal. Information has been collected on the economics of multiple-use marketing of lignite used in cogeneration or steam generation, wastewater cleaning, and/or briquettes, including possible waste solids disposal costs in Grand Forks. The most environmentally acceptable coal-to-steam process is fluidized-bed combustion. Unfortunately, the wastewater treatment multiple-use scheme tested did not make North Dakota lignites more economically acceptable than subbituminous coals. The final report was issued in September 1993.

Task 2 – Seventeenth Biennial Low-Rank Fuels Symposium

The 17th Biennial Low-Rank Fuels Symposium sponsored and organized by the EERC with support from the DOE–EERC JSRP was held May 1993 in St. Louis, Missouri. Other sponsors included the American Coal Ash Association, BNI Coal, Ltd., Knife River Coal Mining Company, MDU Resources Group, Inc., Minnkota Power Cooperative, Minnesota Power Cooperative, Inc., Northern States Power Company, N-R-G Energy, Inc., North American Coal Corporation, Otter Tail Power Company, and Utility Fuels, Inc. The first Low-Rank Fuels Symposium (formerly called the Lignite Symposium) was held in 1961.

Low-rank coals, found in the United States primarily west of the Mississippi River, typically have lower sulfur contents than eastern coals, making them the fuel of choice for utilities faced with more stringent emission standards. Low-rank coals are also likely to play an increasingly greater role in meeting world energy needs. About half of the world's recoverable coal reserves are subbituminous and lignite, or brown, coals. In addition, some of the most populous and rapidly developing countries in the Pacific Rim and East Central Europe have large reserves of low-rank coals that will be used to fuel economic growth. This realization, combined with the awareness in the United States and around the world of our dependence on liquid and gas fossil fuels, provides impetus for renewed research and development efforts focused on clean, efficient use of the world's enormous low-rank coal reserves.

The goal of this biennial international conference is to provide a forum for the exchange of information that can be used to develop efficient technologies to utilize low-rank fuels in an environmentally acceptable manner. The symposium provides for communication, discussion, and dissemination of recent information on low-rank fuel utilization. The symposium brought together members of the energy community from government, industry, and academia with an interest in low-rank coals to share current information on the opportunities that low-rank coals present.

The symposium addressed the need for government, industry, and academia to engage in joint ventures that move key technologies out of the laboratory and into the marketplace. Representatives from Germany, Spain, Australia, Finland, Bulgaria, Korea, Yugoslavia, and the Czech Republic attended the conference. The technical program included sessions on environmental issues, coal quality, conventional and emerging and advanced technologies for low-rank coals, and international market opportunities. Symposium proceedings were published by the EERC in May 1994.

Task 3 – Slagging and Fouling Assessment of a Coal and Coal Chars

A coal and two char–coal blends were submitted to the EERC by the Illinois State Geological Survey for evaluation of fouling and slagging propensity: an Illinois Basin coal (IBC-102), referred to here as "coal;" a char–coal blend made from this coal by a low-temperature oxidation process followed by blending with the original coal, referred to here as "LTO char blend;" and a second char–coal blend produced by adding hydrated lime, oxidizing under high-temperature conditions, and blending with the original coal, referred to here as "HSAHL char blend." A final report was submitted in September 1993.

The following analyses and bench-scale combustion tests were performed:

- Mineral and chemical analysis of the coal to apply advanced fouling and slagging indices
- Thermoequilibrium modeling of predicted slag deposits to predict slag deposit viscosities, which are an indication of the degree of melting and sintering in the slag
- Measured crushing strength of fouling deposits formed in a bench-scale reactor, which is a good indicator of fouling deposit severity
- Mineral- and amorphous-phase compositions and calculated liquid-phase viscosity for fouling deposits generated in a bench-scale reactor, which provides an indication of relative deposit severity
- Initial slagging temperature of a deposit formed in a bench-scale reactor

The following conclusions were drawn on the basis of work performed:

- The chemistries of the IBC-102 coal and LTO char blend are quite similar, dominated by the Fe, Al, and Si content. The LTO char has a slightly lower sulfur content than the IBC-102 coal. The HSAL char blend has a chemistry drastically different from both of them.
- The computer-controlled scanning electron microscope (CCSEM) analysis shows the dominant coal minerals to be quartz, kaolinite, and pyrite. The HSAHL blend contains a significant amount of calcium sulfate as a result of lime addition.
- Comparing the three fuels, all diagnostic tests and calculations show that the HSAHL char blend would cause severe slagging, high-temperature fouling, and, possibly, low-temperature fouling problems. The coal exhibits slightly more slagging and high-temperature fouling behavior than the LTO char blend. The slagging behaviors of both the coal and the LTO char blend are similar to those of an Illinois No. 6 coal and are controllable. As a boiler feedstock, the LTO char blend would be most attractive as a boiler feedstock because of lower slagging and fouling potential, lower sulfur content, and higher Btu content than the parent coal.

Task 4 – Processing Concerns in Thermal Recycling of Waste Materials

The composition of postconsumer plastic streams varies with location, season, and time. Because of the many applications of plastics, numerous additives, both inorganic and organic, are present in the plastic products. Contaminants from use by the consumer will be mixed with the plastics. Processes to recycle plastics will need to account for all of these factors. Processes to recycle polyethylene terephthalate (PET) or high-density polyethylene (HDPE) exist mainly because large enough quantities of feed are available at a sufficiently low price to make the process economical. For most types of plastics, delivery of sufficient quantities to a process dedicated solely to the recycling of that plastic is economically prohibitive. As an additional recycling option, several groups around the United States and in Europe are examining methods of thermal decomposition (sometimes referred to as thermal depolymerization or feedstock recycling) of mixed plastics streams. A range of hydrocarbon liquid and gaseous products are available from this type of process, many of which have potentially large markets. The products of thermal depolymerization can be used for the manufacture of new plastics or various other hydrocarbon-based products.

The EERC, under joint sponsorship of the American Plastics Council, the 3M Company, and DOE, undertook a bench-scale thermal depolymerization process development program that ran from September 1992 to June 1993. Testing was conducted in a 1–4-lb/hr continuous fluid-bed reactor (CFBR) unit using individual virgin resins and resin blends and was intended to determine rough operating parameters and product yields and to identify product stream components. Process variables examined included temperature and bed material, with a lesser emphasis on gas fluidization velocity and feed material mix. The following work was performed: 1) a short program to determine the suitability of using CaO (lime) in a postreactor, fixed bed for chlorine remediation, 2) thermal depolymerization of postconsumer plastics, and 3) testing of industrial (3M Company) products and wastes to determine their suitability as feed to a thermal depolymerization process.

The involvement of DOE in the development of the plastics thermal depolymerization process has helped to facilitate the transfer of coal conversion technology to a new and growing area—waste conversion. These two technology areas are complementary . The application of known coal conversion technology has accelerated the development of plastics conversion technology, and findings from the plastics polymerization process development, such as the development of chlorine remediation techniques and procedures for measurement of organically associated chlorine, can be applied to new generations of coal conversion processes.

Chlorine Removal from the Products of Thermal Depolymerization of Plastics

Thermal depolymerization of mixed-plastics streams will necessarily include some method of removing chlorine, present primarily from the decomposition of polyvinyl chloride (PVC). Chlorine removal can take place before the depolymerization step (feed pretreatment), during depolymerization (in situ), or after depolymerization (postreactor scrubbers). The first phase of this study investigated the feasibility of chlorine removal in a fixed-bed, postdepolymerization scrubber using calcium oxide as a sorbent. Tests using polypropylene (PP) and PVC were performed at three filter temperatures, two depolymerization reactor temperatures, two sorbent particle sizes, and two ratios of PP to PVC in the feed material. The qualitative effects of these variables on total and organic chlorine levels in the product liquids were determined. Concurrent with the evaluation of the feasibility to use a fixed bed of CaO to remove chlorine, tests were conducted to determine the detection limits of organically associated chlorine using the gas chromatography–atomic emission detection (GC–AED) technique. Additionally, a quality control procedure was implemented for the technique.

For the PP/PVC tests, CaO was found to capture between approximately 43% and essentially 100% of the chlorine introduced to the system. The greatest effect on capture efficiency is filter temperature. At both depolymerization temperatures examined (440°C and 540°C), tests in which filter temperatures were maintained at the depolymerization temperatures (prohibiting any condensation of the product liquids) resulted in nearly 100% capture of chlorine by the CaO and prevention of organochloride formation in the product liquids. At 440°C, organic chlorine formation in the product liquids was observed only when the filter temperature was set at 340°C. No organic chlorine formation in the liquid products was observed in the 440°C depolymerization test at a filter temperature as low as 390°C.

While conditions were identified for very good chlorine capture, some chlorine remained in all PP/PVC test product liquids. Two filters placed in series (or a deeper bed) or other combinations of chlorine removal methods placed in series could drop the chlorine level down to acceptable levels (1–2 ppm). These possibilities are areas for future investigation.

Thermal Depolymerization of Postconsumer Plastics

After successful completion of the CaO fixed-bed tests with PP and PVC, similar tests were performed using a postconsumer plastics (PCP) stream to demonstrate the ability to process PCP and to evaluate chlorine capture efficiency of CaO with this type of feed material. Chlorine capture from postconsumer streams is complicated by the presence of water, CO_2, metals, and organic acids, which can block sites used for chlorine fixation, and by particulates (carbon) produced from the decomposition of PET.

While chlorine removal remains a primary concern for a thermal depolymerization process, metals content of the product liquids and leachability of the bed material also need to be addressed. The process of creating product acceptability will need to begin with characterization of these products in terms familiar to end users. For the product liquids, these specifications will include metals content and relevant characterizations. For example, some process conditions produce a liquid that is similar in boiling point distribution to a gasoline. For these liquids, a boiling point distribution, specific gravity, octane number, and PIANO (paraffins, isoparaffins, aromatics, naphthenes, and olefins) analyses might be appropriate. For liquids that resemble a gas oil, a microactivity test might be appropriate.

Thermal depolymerization of postconsumer plastics proved to be generally more difficult than when virgin resins were used as feed materials. The first attempts at processing the postconsumer blend were unsuccessful, so the PCP feed material was blended with HDPE and PP resin. The most likely explanation for the difficulty in processing this material was the high PET content. However, using the postconsumer plastics material mixed with HDPE and PP, the tests were completed.

Tests were completed using postconsumer plastics at temperatures of 440° and 540°C. In addition to dilution with HDPE and PP, because of the high concentration of PET, steam was added, effecting a de-esterification reaction. Results of the tests indicate a good-quality liquid is produced at both temperatures: the liquid product from the 540°C test is similar to a gasoline or naphtha fraction (with 80% boiling below 235°C) and that produced at 440°C is slightly lower in boiling point distribution to a diesel fuel. A PIANO analysis of the liquid produced at 540°C, based on gas chromatography–flame ionization detection (GC–FID) results, revealed that this product is more aromatic than that of a cut of similar boiling point distribution from a petroleum refinery. Organic acids (probably terephthalic and benzoic) and acetophenone were some of the components identified as unique to liquids produced from postconsumer plastics.

In situ chlorine removal is not as efficient with the PCP as with pure polymers. Postreactor chlorine removal in the fixed-bed unit produced chlorine levels in the product liquids comparable to those observed when pure polymers (PP/PVC) were processed using CaO for in-bed capture. In processing PCPs, sorbent chemistry is complicated by the presence of water, CO_2, and metals. Although organic acid fragments and carbon were speculated to be troublesome, they were not. It was determined that, because of the presence of CO_2 from PET decomposition, calcium oxide is converted to calcium carbonate. Calcium carbonate is not effective for chlorine capture at the temperatures of interest. In the 440°C test, when minimal CO_2 was produced, about 15% of the filter material was CO_2 (calcium was associated as carbonate). About 20% of the filter material occurred as $Ca(OH)_2$. In the 540°C test, about 30% of the filter material was CO_2, and no $Ca(OH)_2$ was detected. These results suggest that when significant levels of PET are present in the feed material, a thermal depolymerization process will need to be carried out at low enough temperatures to minimize CO_2 production, or alternatively, the sorbent regeneration rate will be fairly high.

A characterization of the residuals (spent bed material) from the tests was performed and showed higher than acceptable levels of several Resource Conservation and Recovery Act (RCRA) metals, although it is unclear whether these came from the starting bed material or from the postconsumer plastics. The difficulties experienced in the early tries with the PCP blend prompted use of a CaO/equilibrium cat cracker catalyst bed. Earlier work had shown some success with a cat cracker catalyst bed when PET was present. The equilibrium cat cracker catalyst, however, may have contained higher concentrations of metals than anticipated. This material was not analyzed alone, so it is unknown what contribution was made to the metals content of the products by the cat cracker catalyst. In future tests, if such bed materials are chosen, these materials will be analyzed beforehand to ensure that these substances are not introduced into the system by the choice of bed material.

Thermal Recycling of 3M Products

Much of the 3M scrap is polymer-based and may contain significant levels of solids. Because of the solids content and because many 3M products are combinations of two or more types of plastics, traditional recycling methods are inappropriate. For example, about three-quarters by weight of magnetic tape is PET. While technologies exist to recycle PET (hydrolysis, methanolysis), no existing process can accept material with high solids loading, with PET in combination with other types of plastics, or with other organic material (e.g., mineral oils).

The EERC was given the opportunity to investigate the feasibility of recycling selected 3M products by thermal degradation to hydrocarbon liquids and gases. Materials examined included magnetic tape pellets, Scotchpak™ pellets (with both high and low PET content), pelletized polymer sheet material, a face mask skeleton scrap, and three types of reflective tape. Thermal depolymerization tests were performed in the EERC 1–4-lb/hr CFBR system. Eleven products were tested, with forty-two test points attempted. Results of the study indicate that several of the low-PET products can be decomposed to yield a usable liquid, with hydrocarbon liquid yields ranging from 24% to 66% over a temperature range of 475° to 550°C. A high-Btu gas is also produced that could potentially be used for process heat. This option needs further investigation, since buildup of trace contaminants in a recycle loop is a concern. Conversion of high-PET materials focused on terephthalic acid (TA) recovery, since TA may be worth as much as 30% more than the oils produced. Oils produced in the process can either be blended with boiler fuels and used in-house at 3M or sold to a refinery for introduction to a higher-value unit, such as a cat cracker.

Products containing levels of PET greater than 10% were known prior to the study to have limits on their processing conditions. A goal of this program was to help outline these boundaries. Previous work had indicated that processing PET at temperatures above about 600°C resulted in coking and agglomeration in the bed. Processing at almost all temperatures without steam also resulted in a prohibitive amount of coking. Three temperature series of thermogravimetric analysis (TGA) tests with magnetic tape were performed under nitrogen, steam, and methanol atmospheres. The TGA tests indicated that at temperatures below 450°C, residence time required for PET decomposition was too long for the fluid-bed configuration being used. It was thus determined that a minimum temperature of 475°C was necessary for fluid-bed operation.

Several tests were performed in a steam atmosphere in an attempt to convert PET to TA by a reverse esterification reaction. Using steam, PET in polymer concentrations from 10% to 100% was successfully decomposed. TA was produced, with yields ranging from 1% to 110 %. Note that these are yields, not conversions, and that starting PET concentrations ranged from 10% to 100%. While some tests showed respectable TA yields, it was determined that impracticably high steam-to-PET ratios were necessary for the solids and gas residence times tested. The highest TA yields observed were seen when a high-PET Scotchpak™ was processed using a 10:1 water-to-PET ratio. It is not yet known which process condition is responsible for this high yield. Feed composition, residence time, steam-to-PET ratio, bed material, or a combination of factors may be responsible for this promising result. Further testing is needed to investigate the possibility of lower steam ratios. Variations in solid and gas residence times may permit processing at reasonable steam flows.

One magnetic tape test was performed in the CFBR in a methanol atmosphere instead of steam to determine the practicability of methanolysis at elevated temperatures. Again on the basis of TGA results, a temperature of 475°C was chosen as allowing as reasonable residence time for the reactor system being used. Product gas compositions indicated that the methanol readily decomposed to CO and H_2. The methanol decomposition products then may have participated in water–gas shift or steam–carbon reactions or substitution for methyl end groups on the PET, introducing water into the system. More TA than dimethyl terephthalate (DMT), the intended product, was produced.

Both high- and low-PET content Scotchpak™ pellets were processed with minimal difficulties. The high-PET material, processed with an approximate 10:1 steam-to-PET ratio, gave the highest TA yield observed of any product tested. The low-PET Scotchpak™, processed with minimal steam (2:1 and lower), gave much lower TA yields. Gas residence time in the high-PET material tests was much shorter than in the low-PET tests.

The white face mask material, composed mainly of PP and PET, decomposed easily, yielding a liquid similar in composition and boiling point distribution to diesel fuel. Liquid yields ranged from 31 % to 39 % over a temperature range of 500° to 550°C. Face mask material mixed with PP tape was tested at temperatures of 475° and 500°C and found to decompose readily, producing a liquid yield of between 40% and 49%.

A product from 3M's Occupational Health & Environmental Systems Division was tested at 500° and 550°C. While the test at 500°C was successful, resulting in a liquid yield of 51%, the test at 550°C was terminated because of reactor plugging.

Three reflective tapes from the Brownwood, Texas, 3M plant, High Intensity™, Diamondgrade™, and Reflectolite™ were examined. All three tapes proved difficult to feed. CaO was added to the feed material in order to coat the feed particles, decreasing the stickiness and aiding flowability. The two other tapes tested, High Intensity™ and Diamondgrade™, were easily decomposed, producing liquid yields between 24% and 66% over a temperature range of 500° to 550°C.

While several of the liquids produced had boiling point distributions heavier than might be desired for use as a boiler fuel substitute, blending in some proportion may be acceptable using currently known conditions. A residence time study conducted at the EERC using PCPs indicated that a slightly longer gas residence time will lighten the product liquid boiling point distribution considerably. It is not yet known what effect a longer gas residence time will have on PET coking or on TA conversion. While the magnitude of the effects of both gas and solids residence time on TA yield and PET coking are not yet fully understood, much progress has been made since the initial tests in this (3M) study, in which bed coking and plugging were severe.

Task 5 – Sorbent Regeneration from Circulating Fluidized-Bed Combustors

The EERC has completed the Sorbent Regeneration from CFBCs project funded by Community Energy Alternatives (CEA) and DOE. Testing proceeded in three phases. During Phase 1, the EERC successfully demonstrated the effectiveness of pelletizing and recycling fly ash for reducing limestone consumption and solid waste disposal by over 25%. For Phase 2, a bubbling FBC was successfully modified and tested for use as a fluidized-bed material regenerator. For the third phase, cyclic operation of the circulating fluidized-bed combustor (CFBC), pelletizer, and regenerator was investigated, demonstrating a potential reduction in limestone consumption ranging from 65% to 85% for five cycles of testing.

Fluid petroleum coke and limestone used for all EERC testing for CEA were from the same source as utilized by CEA's GWF Power Systems (GWF) CFBC facilities. Building upon the success of Phase 1 testing with pellets made from GWF fly ash, Phase 1B testing proceeded using the fly ash generated during combustion in the EERC 1-$\mathrm{MW_{th}}$ CFBC. The fly ash was collected, pelletized, and recycled to the CFBC to enhance the sorbent utilization. Using only limestone for sulfur capture to establish a baseline condition, 0.37 lb limestone per lb coke (Ca/S ratio of 3.1) was required to achieve 89.9% retention of the sulfur in the coke. For the fourth cycle using EERC fly ash pellets, the limestone consumption was reduced by 21.6% to 0.29 lb limestone per lb coke to achieve 91.7% sulfur retention (Ca/S of 2.7).

Phase 2 shakedown conditions for the regenerator were selected to obtain optimal removal of sulfur from the sulfated bed material. Shakedown tests were successfully conducted with EERC bed material from Phase 1B testing and then with GWF bed material at an average bed temperature of 2150°F. This resulted in about 90% conversion of calcium sulfate to calcium oxide for both types of bed material tested.

For Phase 3 testing, each CFBC test cycle was approximately 24 hours in duration. The spent bed material and fly ash collected from any given cycle were respectively regenerated and pelletized during the following 24 hours before being reintroduced into the CFBC for additional sulfur capture. Fly ash was pelletized in the same manner as for Phase 1B testing. Operational problems were encountered with start-up of the regenerator during the first week of testing. On three separate occasions, the bed agglomerated in the regenerator during start-up. The regenerator was then successfully started using a pure limestone bed. Agglomeration in a full-scale regeneration system could be avoided by using operational procedures demonstrated during this test.

Regenerator thermocouple failures were numerous and at times difficult to detect. Lower-than-actual bed temperatures were indicated when the thermocouple tips burned off in the hot bed and then the thermocouple wires fused together back near the somewhat cooler refractory walls where the thermocouples penetrate the regenerator. As a result of multiple thermocouple failures, the combustor bed material from the first cycle of Phase 3 was subjected to extremely high regenerator temperatures and apparently was ineffective for good sulfur capture. It also appeared that the material generated during shakedown for use during Cycle 1 had been regenerated at temperatures that resulted in ineffective sulfur capture. The EERC CFBC bed was purged of this material at the end of the first week of testing and replaced using limestone as the only sorbent. Testing was essentially restarted back to Cycle 1 for the second week, and the regenerator was operated at 2000° to 2050°F for all of the remaining test periods. Better results were obtained with bed material regenerated at lower temperatures.

Baseline limestone usage for Phase 3 was 0.31 lb limestone per lb coke (Ca/S of 2.9), achieving 89.6% sulfur retention. During the fourth cycle of testing, limestone consumption was reduced by 85.5% to 0.045 lb limestone per lb coke (nearly a sevenfold reduction in limestone consumption) when fly ash pellets and regenerated bed material were used to achieve 89.3% sulfur retention at a total Ca/S ratio of 3.9. The fifth and final cycle, Test 6A, proceeded for the final 8 hours of testing when the 2-week supply of fluid coke was depleted. While there was not adequate time for Test 6A test conditions to fully stabilize, limestone consumption was reduced 65.8% to 0.106 lb limestone per lb coke at 84.3% sulfur retention for a total Ca/S ratio of 4.7. It is unclear if an adequate number of cycles had been performed to approach an overall steady-state condition to accurately establish the addition rate of limestone required with the fly ash pellet and regenerated bed material feed for 90% sulfur capture.

During Phase 1, vanadium and nickel concentrations showed only a slight increase, from 0.44 and 0.15 wt%, respectively, in the combined ash stream for the limestone-only case, to 0.63 and 0.18 wt%, respectively, for the fly ash pellet and limestone feed case. For Phase 3, with limestone, fly ash pellet, and regenerated bed material feed, concentrations of vanadium and nickel had increased to 0.69% and 0.23%, respectively, at the end of the test run.

NO_x emissions and combustion efficiencies were also monitored. NO_x emissions were directly proportional to the ratio of calcium to sulfur for Phase 3 testing and ranged from 50 ppm (corrected to 3% O_2) and 0.072 lb/MMBtu for Test 1A to 117 ppm (corrected to 3% O_2) and 0.168 lb/MMBtu for Test 2A. Measured combustion efficiencies at about 98% were similar to Phase 1 results. Combustion efficiencies would probably approach 100% with sustained operation, as any fly ash carbon would be recycled to the CFBC in the form of pellets and any bed material carbon would be consumed during the regeneration process.

It is uncertain how limestone consumption would be affected with continued cycles of testing. Although the pilot-scale tests clearly demonstrated a significant reduction in limestone consumption by combining fly ash pelletization and bed material regeneration, it is doubtful that the test was of long enough duration to reach a true steady-state condition. A longer continuous operation is recommended to better quantify the benefits of this process. It would also be extremely useful to more completely understand the regeneration process so that optimum bed material sulfur removal could be obtained during regeneration without significantly degrading the sulfur-capturing properties of the material when it was reused in the CFBC.

Task 6 – Evaluation/Interpretation of Rocky Mountain 1 Data

This task included five projects, four of which were supported by DOE–EERC JSRP funding. Summaries of the final reports are given below for the four JSRP projects.

Detailed Evaluation of Process and Environmental Data from the Rocky Mountain 1 Underground Coal Gasification Field Test

This assessment of the Rocky Mountain 1 (RM1) underground coal gasification (UCG) test results provides 1) a better understanding of process:site interaction, important to optimized design and siting of future UCG operations; 2) a more refined material and energy balance methodology which will allow a more accurate evaluation of future UCG operations; and 3) recommendations for the further refinement and optimal application of the UCG methodology. In addition, this analysis has confirmed that innovative RM1 design features such as operating at low pressures and postburn cavity venting and cooling are effective in terms of conducting UCG in an efficient and environmentally sound manner.

Leaching and Attenuation Characteristics of Unaltered and Thermally Altered Materials from the Rocky Mountain 1 Underground Coal Gasification Field Site

This report reviews the results of an experimental leaching and attenuation investigation involving unaltered and thermally altered geological materials from the RM1 UCG field test site near Hanna, Wyoming. Short- and long-term leaching experiments revealed that the potential for a variety of inorganics to be introduced into groundwater by leaching from thermally altered geological materials at the RM1 site was very limited and that significant water quality impacts involving those inorganics were unlikely. At the same time, the attenuation experiments indicated that both unaltered and thermally altered RM1 materials had notable capabilities to mediate the removal of a variety of trace elements, particularly heavy metals, from groundwater. A comparison of the experimental results with the groundwater chemistry data collected from the RM1 site suggested that laboratory-based leaching and attenuation activities utilizing site-specific conditions and materials have some predictive value. Furthermore, the results proved valuable for contributing to an understanding of the source, transport, and fate of inorganics, including a number of potentially problematic species, at the RM1 site. It was, therefore, recommended that leaching and attenuation experimental activities be considered for inclusion in all future UCG siting, design, and evaluation efforts.

Atlas of Minerals and Related Phases in Unaltered and Thermally Altered Materials from the Rocky Mountain 1 Underground Coal Gasification Field Site

This document provides information, data, and insights that will be particularly useful in identifying and establishing the significance of mineral, quasi-amorphous, and amorphous phases in geological materials recovered as part of future efforts to select suitable UCG sites, design and conduct successful UCG operations, and evaluate those operations after they have been completed. This compilation is intended to provide users with diagnostics and RM1 characterization results that, together, enable them to make soundly based preliminary decisions regarding the identity and significance of individual phases that are the same as, or related to, those found in the RM1 study materials. Specifically, the document consists primarily of 52 alphabetically arranged sections in which the 63 phases identified in the RM1 pre- and posttest study materials are treated in a consistent, user-friendly format. A companion report involving the same authors reviews the design, conduct, and results of the characterization activities that served as the basis for the development of this document.

Characterization of Thermally Altered Materials from the Rocky Mountain 1 Underground Coal Gasification Field Test in Wyoming

The RM1 UCG field test was conducted near the town of Hanna in Carbon County, Wyoming, from November 16, 1987, to February 26, 1988, under the sponsorship of Amoco Production Company, Union Pacific Resources, and EPRI as well as DOE and GRI.

The effort to address the issue of the use of horizontal process wells involved the simultaneous testing of two UCG process configurations, namely, the extended linked well (ELW) configuration, with vertical injection wells and a horizontal production well, and the controlled retracting injection point (CRIP) configuration, with horizontal injection and production wells. The test design also incorporated assessments of the effects of different steam:oxygen ratios and oxygen injection rates on gas quality and provided for the acquisition of a wide range of significant test-related data.

The enormous amount of data that resulted from the detailed physical, chemical, and mineralogical characterization of geological materials recovered from in and near the RM1 UCG cavities served as a basis for delineating the UCG-related thermal history of the RM1 site, as well as the underlying thermal transformations. During this characterization of unaltered and thermally altered inorganic materials from the RM1 site, a framework was developed that enabled resulting observations and data to be used to identify the extent to which the recovered samples had been thermally altered. Specifically, this framework was composed of six successive temperature increments covering the range experienced by the study materials. These increments, or stages, were defined on the basis of the results of previous thermal alteration studies in several disciplines and the preliminary results of this effort. Not only did the framework provide an extremely useful working tool that allowed the extent of thermal alteration to be readily delineated, but it also, in its refined form, provides a reasonably comprehensive history of thermal alteration at the RM1 site. Although, in its specifics, this framework is not directly applicable to other UCG sites because of variations in geology, operational conditions, etc., it, nonetheless, represents an approach that is universally applicable and should be seriously considered for use by future UCG site investigators.

Task 7 – Agglomeration and Deposition in FBCs

Partners with DOE and the EERC in this task included Foster Wheeler Development Corporation (formerly Ahlstrorn Pyropower, Inc.), the Industrial Commission of North Dakota, Northern States Power Company, Riley Stoker, and EPRI. A final report was submitted in February 1996.

The successful design and operation of a fluidized-bed combustor (FBC) requires the ability to control and mitigate ash-related problems. The major ash-related problems in fluidized-bed combustion are agglomeration of bed material, ash deposition on heat-transfer surfaces, ash deposition on refractory and uncooled surfaces, corrosion, and erosion. The focus of this program was on the agglomeration and deposition problems in atmospheric bubbling and circulating beds. This 3-year, multiclient program was designed to determine the behavior of inorganic components in FBC units using advanced analytical methods coupled with bench-scale combustion experience.

To diagnose and reduce ash-related problems in FBC systems, a comprehensive understanding of the fuel, ash, and system materials properties must be achieved. This understanding requires that the materials be analyzed in detail to assess their chemical and physical characteristics. Effective materials analysis requires appropriate and effective materials-sampling techniques. Because materials sampling must often be undertaken by operations personnel, it is important that a standard sampling method be available. Therefore, a sampling and analysis protocol was developed to aid the operations engineer in providing effective samples for analysis and testing. This protocol is organized to provide a handy reference for those involved with FBC operations.

Full-scale sampling yielded many interesting and useful results. An intensive sampling effort was undertaken at the Montana– Dakota Utilities 80-MWe bubbling bed facility located at the Heskett Station. Agglomerating tendencies at this unit force a bed turnover approximately every 50 hours. Deposition on the superheater surfaces results in a loss in superheat of over 40°F during the course of 4 months. The analysis of the data from the Heskett Station shows conclusively that certain coal ashes tend to form deposits in the FBC. The mechanisms of adherence and growth appear to be via a molten sulfate matrix, through the fluxing action of sodium with the calcium sulfate matrix. The bed material plays no significant role in the deposition matrix. The agglomeration, on the other hand, shows a definite interaction between bed material and ash, with certain minerals in the bed contributing more to agglomeration than others.

Ten different fuels have been tested in the EERC 1-MWth CFBC under separate programs. The tendency for each of the fuels to form deposits and agglomerates in the CFBC pilot plant was evaluated as a part of this program. Agglomeration was less prevalent than deposition and was noted only for the Center lignite and petroleum cokes. The agglomeration for the Center lignite was undoubtedly related to the sodium content in the lignite. It is less clear what initiated the agglomeration in the petroleum coke cases; however, it is speculated that local reducing conditions provide the opportunity for low-temperature eutectics of either CaS and $CaSO_4$ or possibly $CaS0_4$ and V_20_5 to form.

Some deposits were formed during firing of most of the test fuels. Deposition occurred on the refractory surfaces of the primary cyclone and downcomer and on the ash-fouling probes that were designed to simulate the leading edge of the convective pass. Generally speaking, the deposits consisted of fine-grained (1- to 10-micron) calcium sulfate. In many cases, the deposits were soft and would slough off of the surfaces because of their own weight. A notable difference was the degree of sulfation of the deposited material. In all cases, the deposit was more sulfated than the ash collected in the secondary cyclone. Deposits formed when high-sulfur fuels were fired were more sulfated than those from low-sulfur fuels. It was also observed that the more-sulfated deposits tended to show higher strength than the less-sulfated deposits.

The following hypothesis is provided on deposit formation. The mechanisms of formation for the thick back side deposits are likely eddy impaction and thermophoresis. Mostly small particles of less than 10 microns follow the stream lines around the tubes and impact as a result of eddy currents. It appears that the primary component of the deposit is partially sulfated limestone. The cementing agent loosely holding the deposit particles together appears to be partially sulfated limestone that continues to become more fully sulfated over time, resulting in continued particle growth. The deposit probably reaches an equilibrium size, at which time it falls off under its own weight. It does not seem that the large deposits on the back side of the probes would represent a serious fouling problem. They are relatively soft, although they could become a hard deposit if permitted to stay on the boiler tubes for an extended period of time. It would seem prudent to at least leave room in the higher-temperature regions of the convective pass for the installation of sootblowing capabilities. The hard deposits on the front side of the probes would be more difficult to remove.

Parametric testing on a bench-scale reactor was performed. A high-sodium lignite was used to generate significant changes in bed chemistry, ranging from coated bed material and particle sticking to a sintered mass causing defluidization, in a relatively short period of time. The effects and interactions of temperature and excess air have been studied. The bench-scale reaction provides a useful tool to study bed chemistry in FBC and can be used to predict agglomerating tendencies.

A laboratory sintering apparatus was used to help understand the chemical and physical characteristics of the coal ash and bed material that lead to agglomeration. Ash generated from the FBC of various coals was tested, with shrinkage (sintering) apparent at 875°C (1600°F) for a highly agglomerating Beulah lignite. Other tests demonstrated the importance of the form of the sodium, by showing an independence of bed sodium concentration and sintering temperature. Fundamental evaluations also showed the existence of a temperature window (788°to 843°C [1450° to 1550°F]) where agglomeration did not readily occur. The influence of $S0_2$ on agglomeration was also demonstrated, with the formation of sulfates being a critical step in the agglomeration process.

Factors that enhance the formation of agglomerates include local reducing conditions in the bed; high temperature, particularly at the surface of coal particles, which approaches the melting temperature of various mineral phases; increased pressure, which speeds reaction rates as a result of increased partial pressure of oxygen; and the presence of a fluxing agent, such as sodium or calcium, which lowers the melting point of certain silicate-based clays. The lignites burned at the Heskett Station and in the bench-scale reactor showed plastic characteristics, which are the probable cause of egg-type agglomerates. Detailed mechanisms of this complete process are provided in the report.

Methods to predict the effect of coal properties and operating conditions on deposition have been developed for conventional coal-fired systems. Existing models and indices were adapted to predict deposition potential in fluidized-bed systems. The emphasis of the computer program FBCDEP is on the prediction of methods of ash formation, partitioning of ash out of the bed, and deposition and deposit strength in the convective pass. The propensity for agglomeration can be predicted based on ash properties using FBCSUL, a code developed during the project, or by firing the fuel in the bench-scale reactor.

In summary, several physical tests were developed as a part of this program that will predict the nature of these ash-related problems prior to the design of a new unit or to a fuel switch in an existing unit. These methods include:

- Testing on a bench-scale fluid-bed reactor.
- Laboratory sintering of ash generated under FBC-like atmospheres.
- Pilot-scale tests.
- Full-scale sampling during short trial burns.

Several protocols and analytical procedures were developed to aid the operations engineer in providing effective samples for analysis and testing. These include:

- FBC Sampling and Analysis: Protocols to Aid in the Prediction and Control of Ash Related Operational Problems.

- Advanced scanning electron microscopy (SEM) procedures for investigating bed particle coating and agglomerates.

Two additional tools that can be used to predict agglomeration and deposition in FBC systems are the computer models FBCSUL for predicting the tendency for a fuel to agglomerate and FBCDEP for evaluating the depositional characteristics of a fuel–sorbent combination.

Task 8 – Development of a Fireside Performance Index: Convective Pass Fouling and Fly Ash Collectability

Industrial partners in this task were Union Electric, Northern States Power Company, Minnesota Power, EPRI, and Kansas City Power & Light. A final report was issued in November 1995.

Advanced indices have been developed by the EERC for predicting coal-related aspects of power plant performance, including main furnace slagging, convective pass high- and low-temperature fouling, slag tapping, sootblowing effectiveness, stack plume opacity, boiler erosion, and coal grindability. The parameters required to calculate the indices consist of coal analysis results determined by CCSEM and chemical fractionation methods, in addition to standard American Society for Testing and Materials (ASTM) proximate, ultimate, and coal ash chemical analysis methods. Boiler specifications and operating conditions, such as the boiler type (pulverized coal or cyclone), combustion conditions (conventional or low-NO_x), maximum continuous load rating, current operating load, and furnace dimensions, are also used as input parameters. The eight indices are expressed numerically as whole numbers ranging from 1 to 100. General classifications of low, medium, and high propensity are assigned to the following specific ranges of index values: 1 to 33, 34 to 66, and 67 to 100, respectively. A greater value corresponds to an increase in severity or adverse effect for a given index. This propensity-index classification scheme applies to all the indices except the coal grindability index. The coal grindability index is directly related to the ASTM Hardgrove grindability index.

The ash deposition indices (slagging and high- and low-temperature fouling) were formulated from existing bench-, pilot-, and full-scale combustion testing data and knowledge of inorganic transformations, entrained ash formation, and ash deposition. Additional bench-scale testing in drop-tube furnaces (DTFs) was performed on eight Powder River Basin (PRB) subbituminous coals to refine and verify the ash deposition indices and to develop ash removability indices (slag tapping and sootblowing). The following combustion conditions were simulated during the testing: slagging, conventional and low-NO_x high-temperature fouling, and conventional and low-NO_x low-temperature fouling. Deposit growth rates, sticking coefficients, in situ adhesion strengths, crushing strengths, initial slagging temperatures, porosities, and chemical and phase compositions were determined. In general, the low-NO_x combustion conditions produce high-temperature fouling deposits that have less adhesion and crushing strengths relative to those produced in conventional combustion conditions. The combustion conditions, however, did not affect the relative strengths of the low-temperature fouling deposits for a given coal. Deposit porosity was found to be a poor indicator of crushing or adhesion strength.

The scattering of light by fine ash particles was the primary mechanism considered in developing the stack plume opacity index. Fine ash fractions, <2 µm in diameter, collected during bench-scale testing of eight PRB subbituminous coals, were analyzed using CCSEM. Advances in particulate sample preparation methods enabled the CCSEM analysis of individual ash particles with submicron diameters as small as 0.1 µm. The fine ash samples produced from the conventional combustion of coal consisted of discrete spherical particles, whereas particle agglomerates were characteristic of the low-NO_x ash samples. Particle-size distributions of the low-NO_x fine ash fractions were coarser because of the agglomeration. Theoretical light-scattering calculations indicate that, for a given coal, the ash produced in low-NO_x conditions generally causes less opacity as compared to conventional combustion conditions. The following phases were abundant in the ashes: Ca aluminosilicate, Ca aluminate, aluminosilicate, silica, (Ca,Mg)O, $CaS0_4$, Na_2SO_4, and (Na,K)Cl. Primary mechanisms that produced the fine ash include the thermal metamorphism of small, <5-µm, mineral grains and the vaporization and subsequent condensation of organically bound Na, Mg, and Ca. Empirical equations for estimating the concentration of fine ash produced from burning subbituminous coals were formulated into an opacity index based on CCSEM coal mineral and fine ash analysis and on DTF testing results. The effects of combustion conditions (conventional or low-NO_x) on fine ash formation and ash electrical resistivity on electrostatic precipitator collection efficiency are also considered in the index.

A grindability index was developed by investigating the relationship of selected coal properties to the measured Hardgrove grindability index for ten subbituminous coals and a lignite coal. Grindability correlated best to the total sulfur ($r^2 = 0.845$) and ash ($r^2 = 0.694$) contents of the coals. The grindability index was derived from a multiple regression analysis of the ash and total sulfur variables. Coal rank (calorific value), moisture content, quantitative included–excluded mineralogy, and maceral compositions of the coals were not significantly correlated to the Hardgrove grindability index.

An index for comparing the relative erosiveness of coals was derived based on the quantity of quartz and pyrite grains that are excluded from coal macerals and range in diameter from 5 to 50 µm. CCSEM and digital image analysis techniques are used to obtain this information. The velocities of quartz- and pyrite-derived ash particles during transport in flue gas and relative mineral hardness are also considered in the index.

A primary goal was to develop more reliable slagging and fouling indices as well as an opacity index for comparing PRB subbituminous coals. Consequently, verification testing of these indices was conducted using eight full-scale utility boilers. Visual assessments of slagging and fouling and measurements of opacity were in general agreement with propensity index classifications (i.e., low, medium, and high).

A computer program designated as the Predictive Coal Quality Effects Screening Tool (PCQUEST) was developed for calculating and displaying the index values. Index values for multiple coals can be presented and compared in a tabular or graphical format. A coal-blending option enables the blending of two to four coals in proportions specified by the user. PCQUEST is most useful for comparing the relative fireside performance of two or more coals or for determining optimum coal-blending strategies. A database of 66 coal analysis files is included with the program.

Task 9 – TRDU Construction

This task was canceled.

Task 10 – Timing of Deposition of Uppermost Cretaceous and Paleocene Coal-bearing Deposits in the Greater Glendive Area, Montana and North Dakota

With the aid of a grant from the National Geographic Society, a cooperative agreement with the State University of New York at Stony Brook, and the EERC–DOE JSRP, Late Cretaceous and Paleocene geologic and paleontologic field studies were undertaken in Makoshika State Park and vicinity, Dawson County, Montana. This region was chosen as a study area because of its potential for yielding new fossil localities and extensive exposures both above and below the K/T boundary, as suggested by previous research by David W. Krause and Joseph H. Hartman. Related field studies were also undertaken in areas adjacent to the Cedar Creek Anticline in North Dakota. This work was part of ongoing research to document change in the composition of mammalian and molluscan faunas during the Late Cretaceous and Paleocene and to relate observed patterns to floral and invertebrate changes in composition. A final report was submitted in February 1996.

This study focuses on the record of mammals and mollusks in the Makoshika stratigraphic section and places old and new observations into a paleomagnetic and palynomorph framework. Of particular interest is the appearance and diversification of archaic ungulate mammals. Simultaneous dinosaur extinction with ungulate radiation has been invoked in gradual, as opposed to catastrophic, models of faunal change at the K/T boundary. However, supposed Cretaceous localities bearing archaic ungulates and other mammals of "Paleocene aspect" may be the product of faunal reworking. Elsewhere in the Williston Basin (e.g., Garfield and McCone Counties, Montana), the molluscan record of uppermost Cretaceous and Paleocene strata indicates the extinction of all of the highly sculptured unionid bivalves just prior to the onset of coal swamps and subsequent coal formation. This event does not appear to be exactly coincident with the K/T impact event and thus may be associated with a large-scale environmental change in some way related to events leading to coal-forming conditions.

The 1993 field season was concerned with the discovery of new mammalian and molluscan localities and the development of a stratigraphic framework for the study. Efforts in 1994 resulted in additional discoveries and large samples of mammalian fossils by concentrating collection activities on the most productive localities. Samples of fossil mammals now have been recovered from new localities of Late Cretaceous and Paleocene age. Of particular significance was the discovery of Hiatt South Locality, which represents a highly productive facies lateral to the previously known Hiatt Locality (early Paleocene). In addition to surface collection, approximately 2200 kg of matrix were processed for fossils.

The mammalian fauna recovered from horizons in the Upper Cretaceous Hell Creek Formation (Lancian) of Makoshika State Park and vicinity resembles faunas from elsewhere in Montana and Wyoming of Lancian age (Lance Creek and Flat Creek) in composition more than faunas in Alberta and Saskatchewan (Trochu and Gryde). At Makoshika, pediomyid marsupials are diverse, and the multituberculate *Meniscoessus* is abundant. No eutherians and only one peradectid marsupial, *Turgidodon rhaister,* have been recovered from these horizons. The mammalian fauna recovered from the lower part of the Paleocene Ludlow Formation resembles other northern latitude Puercan faunas in composition. This fauna includes the multituberculates *Neoplagiaulax, Stygimys,* and *Ectypodus?,* the primitive taeniodont *Onychodectes,* and a diverse assemblage of archaic ungulates, including species of *Baioconodon, Eoconodon, Loxolophus, Tinuviel,* and *Oxyacodon.* From the upper part of the Ludlow Formation, the School Well local fauna (Torrejonian) is known as yet from fewer specimens than the other localities. It contains the plesiadapiform *Paromomys sp.,* the multituberculate *Ptilodus montanus,* and the condylarths *Promioclaenus sp.* and *Litaletes* sp.

Strata yielding typical Late Cretaceous mammals are separated from those yielding early Paleocene mammals by about 20 in. The K/T boundary in this interval was recognized on the basis of palynomorphs through work conducted at the EERC. Pollen studies also recorded the preliminary identification of the fern spike, noted elsewhere by others as a K/T boundary event. Lack of any type of Bug Creek vertebrate assemblage suggests that the controversial "Bugcreekian" biochron need not be extended into this area. This implies that the adaptive radiation of archaic ungulates may not have begun until after the dinosaur extinction.

Also in 1993 and 1994, sediment samples were taken for paleomagnetic analysis. Lithic samples for paleomagnetic analysis collected in 1993 (Section M6723) did not provide a clear or unambiguous signal of the sequence of paleomagnetic reversals. Sampling in 1994 (Section M7887b), however, permitted the identification of Chron 30n, Chron 29r, and Chron 29n. The results of the analyses of these samples confirm the palynomorph identification of the K/T boundary in Chron 29r. The study of the record of reversal stratigraphy also provides a concordant temporal framework to provide additional strength to interpretations regarding mammalian age determinations, placing the middle lower Paleocene mammalian faunas in Chron 29r.

The record of mollusks in Makoshika State Park is poor to virtually nonexistent. A few specimens of little value were collected from the Cretaceous-age Muddy Tork and Q.V. Localities and Locality L6467, the lowermost Paleocene-age Locality L6260 (just above the Contact lignite), and from the lower Paleocene Hiatt South and Deer Crash Localities and Locality L6425, both of which are at the same level. Most of the specimens are steinkerns of small specimens of mesogastropods of the families Pleuroceridae and Viviparidae. Specimens questionably identified as New Genus A *limneaformis* (family *incertae sedis)* were found both below and above the K/T boundary. Freshwater bivalves are represented by only a few specimens. One pisidiid is known from the Hell Creek Formation, and unionid impressions occur just above the Contact lignite. Although of limited systematic or biostratigraphic value, this depauperate fauna is representative of the limited species diversity found at many localities in the lowermost Paleocene in North America.

Task 11 – Coal Agglomeration Consortium

The commercial sponsor withdrew from this project before work commenced, and the allocated DOE–EERC JSRP funds were not expended.

Task 12 – Formulation and Evaluation of Controlled Low-Strength Materials Utilizing Byproducts from Montana–Dakota Utilities

This project was canceled.

Task 13 – Phenol Purification Studies

Phenolics are major liquid products obtained during the gasification of coals. Unfortunately, they are not recovered as pure compounds, but contain a wide range of contaminants, including neutral oils and basic nitrogen compounds. On the open market, the cost and purity of the phenol dictate the marketability of the product. Dakota Gasification Company (DGC) has a strong interest in reducing the cost of upgrading to produce purer phenol that can be more readily marketed. DGC requested that the EERC perform confidential high-risk preliminary feasibility tests on a number of possible purification methods followed by parametric studies on methods that showed promise. A variety of techniques were investigated, including extraction, distillation, and reaction methods. The ultimate goal was the identification of commercially viable techniques to produce pure phenols from the phenolic streams produced during coal gasification. Four short confidential reports were submitted to DGC.

The simple conclusion from this study is that some reactive species can be destroyed, but this is often accompanied by the production of other compounds. Stable compounds are not affected. The azeotropic distillation or catalyzed polymerization methods tested resulted in only a very limited reduction of total neutral oils (verified by both EERC and DGC analysis).

The principal investigator of this project monitored it closely to ensure that work was not performed until approved by DGC. This meant taking personnel away from the project until approvals were obtained, resulting in project delays. The only work performed without prior approval, and which was never approved, was the development of the extraction method to determine impurities in phenol (the researcher did it on his own time). A final report was submitted in December 1994.

Task 14 – Effect of Ethanol Denaturant on Gasoline RVP

The CAAA of 1990 require further reduction in gasoline Reid vapor pressure (RVP) to reduce pollution. This research cosponsored by the National Corn Growers Association focused on characterizing the effect of ethanol denaturant and water on the RVP of the final ethanol-blended fuel. Anecdotal stories tell of up to a 0.5-psi effect of ethanol denaturant on the RVP of the finished ethanol-blended gasoline. Additionally, earlier EERC data indicated water could have a significant effect on RVP. It was necessary to scientifically verify these effects using acceptable laboratory protocols. A final report was submitted in December 1993.

Environmental Protection Agency. An important aspect of this study was the development of the laboratory testing procedures that will lead to data acceptable to rule-making organizations such as EPA. We maintained a dialogue with the EPA to ensure acceptable laboratory protocols.

Denaturants. The *Code of Federal Regulations* (27 CFR 21) specifies the alcohol denaturants authorized for fuel uses. Of these, we selected unleaded gasoline, rubber hydrocarbon solvent (natural gas liquids), kerosine, and methanol for use in this study.

Experimental design. The first series of tests established the base RVP and water content of the starting ethanols, natural gas liquids, regular unleaded gasoline, methanol, and kerosine. Since many prior gasoline studies have been based on Indolene HO III as a model fuel for unleaded gasoline, our second test matrix used indolene to produce E10 blends. The form of the indolene matrix was repeated with a local sample of regular unleaded gasoline obtained "at the pump" as the third matrix. The fourth experimental matrix was performed on a premium unleaded gasoline. As the magnitude of the water effect became apparent, additional water tests were performed. EPA's Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan, supplied its current standard gasoline, "CAA Baseline gasoline."

Four definite and scientifically significant conclusions can be made:

1. In all cases (nine experimental series) where water was added to an ethanol blend, the RVP increased. This positive influence on RVP may indicate that the existing body of RVP data drawn from at-the-pump fuels may include an unknown measure of water-induced vapor pressure.

   For any sampling of at-the-pump gasolines, it is reasonable to expect a certain degree of water contamination. However, the use of gas-line antifreezes acknowledges the issue of water contamination in many gasoline situations, not just those concerning ethanol blends.

2. The different denaturants used in this study produced different final RVPs. While the magnitude of the denaturant effect did not meet anecdotal stories, the differences were significant. It can be concluded that a better matching of the denaturant to the base fuel

will lead to a reduction in the overall average RVP of E10 fuels. Insufficient data are available to allow us to determine the best choice of denaturant.

3. From weathering tests of the EPA CAA Baseline gasoline, removal of little more than 1% of the fuel volume resulted in the reduction of the base RVP by 1 psi. This result could have a profound effect on the impact of fuel weathering and commingling.

4. The use of incrementally larger amounts of ethanol (in the E12 to E15 range) may yield a further reduction in RVP. While this improvement is likely to only be around 0.1 psi, any area for RVP improvement should be considered.

From our initial statistical analysis, significant differences appear to be justified for changes as small as 0.1 psi. This is lower than the generally accepted 0.3 psi.

Task 15 – Process Development Unit Test Program for Thermally Recycled Plastics

The EERC has developed a mixed-waste plastics thermal depolymerization technology that uses a fluid-bed reactor system to yield a suite of marketable products. Over 200 tests were performed with the EERC 4-lb/hr CFBR, and the EERC 100-lb/hr process development unit (PDU). A final report was submitted in August 1996.

The basic challenge for plastics recyclers is to economically produce marketable commodities such as high-purity olefin monomers for recycled polymer production or a chemical/refinery feedstock. Under current economic constraints, advanced recycling, which involves costs associated with collection, cleaning and sorting, shredding and sizing, processing, and byproduct disposal, is at best marginally cost-competitive with manufacturing plastics from virgin resin and disposing (via incineration or landfilling) of used plastics. For these reasons, the EERC has focused on process and product optimization in the following areas:

Value-added products. To maximize economic viability, process optimization efforts have been based on maximizing yields of one or more of three value-added products:

- A halogen-free liquid hydrocarbon stream suitable for processing as a chemical/refinery feedstock
- A high-purity light-olefins stream containing ethylene, propylene, and butylenes for production of recycled polyolefins
- High-purity terephthalic acid for production of recycled polyethylene terephthalate

Process robustness. To minimize costly preprocessing steps such as cleaning, sorting, and sizing, emphasis has been placed on development of a robust process that will handle the wide variety and concentration range of materials that make up waste plastic mixtures.

Manageable byproducts. To minimize byproduct management costs, process development efforts have been based on incorporation of technologies for on-line chlorine (and other halogen) capture and recovery and quantitative recovery of heavy metals as dry particulate.

A large number of virgin, postconsumer, simulated postconsumer, and postindustrial plastics were tested for product yields under a variety of process conditions, including temperature, gas residence time, and bed material. The highest-value-products, light olefins, were produced at a 35% yield from a postconsumer stream that contained 20% PET. Tests with base blends produced light-olefin yields of 45%–50%, with an additional 30% as liquid organics. Temperatures for these yields were 650°–700°C at gas residence times of 6–15 seconds.

For organic liquid production, temperature has the greatest effect on product yields and characteristics; gas residence time has a lesser effect. Liquid yields will decrease from over 90% at temperatures below 500°C to 30% at 700°C. The quality of liquids can be changed from highly olefinic/aliphatic to cyclic to aromatic by increasing temperature. Higher gas residence times produced lighter liquids. The feedstock also has a great effect on the quality of liquids and the ability to process the material. Polystyrene promotes aromatic liquid production, and PET, which requires water for hydrolysis, may hinder reactor operation at lower temperatures.

Approximately 30% of the PET of a 50% PET stream can be converted to TA, with smaller additional yields of benzoic acid and benzene compounds. Although it appears that the highest TA yields are achievable with low-temperature hydrolysis, high-purity TA feedstocks are required, whereas the EERC high-temperature hydrolysis process can be applied to highly mixed postconsumer feedstocks.

Many postconsumer feedstocks contain 5% or more PVC. The chlorine can be effectively removed from the system using CaO, yielding an organic liquid (condensate) product containing chlorine at levels of less than 100 ppm (with a target value being less than 200 ppm).

While the technical results from the past 4 years of bench-scale and pilot plant testing have shown that postconsumer plastics recycling for production of chemical feedstocks can be accomplished, economic viability remains marginal because of low crude oil prices, low landfill costs, and reduced public pressure for recycling. Oil prices have remained steady, with new technologies such as horizontal drilling finding new reserves and with stable supplies in the Middle East. Landfill costs are rising but not as quickly as predicted. A Title D landfill is very cost-competitive with other options. Material recycling facilities are also separating products for use in the recycling marketplace. Environmental issues have taken a back seat to federal deficit and health care issues, which have become the current focus of national attention. Until these issues become less prominent, motivation for recycling, and in particular, tertiary recycling, will remain low.

Task 16 – Bench-Scale Preparation and Combustion of RDF–Lignite Slurry Fuels

Batch experiments using the EnerTech–EERC wet carbonization process were conducted with three different slurries: a refuse-derived fuel (RDF), a North Dakota lignite slurry, and a blend of North Dakota lignite and RDF. After the slurry carbonization treatment, all three slurries were concentrated and combusted in a bench-scale pressurized fluidized-bed combustion (PFBC) unit. A final report was submitted to DOE and commercial sponsor EnerTech Environmental, Inc., in November 1994.

Rheological profiles conducted on the feed and carbonized RDF slurry indicated an increase in solids loading at a slurry viscosity of 500 cP, from 10 wt% solids to over 45 wt% solids after the carbonization process. In addition, chloride concentrations were reduced by over 80 wt% in the carbonized RDF slurry. Slurry carbonization studies for lignite indicated that the slurry heating value was increased by over 60%, with an achievable solids concentration of 55 wt%. Also, sulfur concentration was reduced from 1.8 to 1.3 wt% (moisture-free) for the carbonized lignite slurry. Results from the blended carbonized RDF and lignite slurry indicated a fuel with a higher heating value of 12,700 Btu/lb (moisture-free), which could be slurried to approximately 57 wt% solids with a viscosity of 500 cP, producing a slurry fuel with a 220% increase in energy density.

PFBC combustion results indicated that all three fuels obtained excellent combustion efficiencies, exceeding 99.0%. Sulfur dioxide emissions were significantly lower for the carbonized RDF slurry (0.10 lb/MMBtu) than for the carbonized lignite slurry (0.62 lb/MMBtu). The nitrogen oxide emissions were slightly lower for the carbonized RDF slurry (0.18 lb/MMBtu) than those experienced from the carbonized lignite slurry (0.24 lb/MMBtu), because of the lower fuel-bound nitrogen in the RDF. For all three carbonized slurry fuels, sulfur dioxide and nitrogen oxide emissions levels were well below current federal regulations. Carbon monoxide and hydrocarbon emissions appeared to be slightly higher for the carbonized RDF and blended carbonized RDF than for the lignite slurry, but were still below 9 ppm.

Task 17 – Enhanced Air Toxics Control

This project was conducted by the EERC for EPRI and DOE to investigate the use of sorbents injected upstream of a particulate control device as a means of controlling mercury from coal-fired boilers. The work was funded under two EPRI work orders: the first, titled “Enhanced Air Toxics Control,” was funded under EPRI WO-3453, and the second, titled “Mercury Sorbent Evaluation,” was funded through EPRI WO-8505. The DOE portion of the projects was funded through the DOE–EERC Cooperative Agreement under Task 17, Enhanced Air Toxics Control, and under Task 40, Mercury Sorbent Evaluation. Research under the combined work orders was conducted as a single project. The overall project, initiated in December 1992, was modified several times to include additional work and address changing research needs. Detailed results have been reported in monthly reports, project review meetings, published conference papers, and other interim reports.

Capture of Mercury by Fly Ash

Pilot-scale combustion tests with all three of the coals resulted in some natural capture of mercury by the fly ash. This was demonstrated by both the Method 29 sampling filter and by the baghouse. In all cases for the same coal sample, the capture increased with decreasing temperature. For the two subbituminous coals, the fraction of Hg^0 decreased when there was more fly ash mercury, implying that it was Hg^0 that collected on the fly ash. For both subbituminous coals, significant natural capture occurred even though the fly ash loss on ignition (LOI) was less than 1%, indicating that high-LOI ash is not necessary for natural mercury capture. For the Blacksville coal, the level of Hg^{2+} decreased with increasing fly ash mercury, implying that Hg^{2+} was collected on the fly ash. The Blacksville fly ash had considerably higher LOI (3% to 7%) than the subbituminous ashes. The implication is that the mercury collection mechanisms are different between the subbituminous and bituminous coals. However, the collection mechanisms are not well known.

Pilot-Scale Testing of Sorbents

Initial screening of six different sorbents showed that the lignite-based activated carbon (LAC) and iodine-impregnated carbon (IAC) were the most effective. Further tests with Absaloka subbituminous coal showed that IAC was highly effective, achieving over 90% total mercury removal at 300° and 400°F. However, with the Comanche subbituminous coal, the IAC was completely ineffective, providing no net mercury removal over the baseline case. The IAC appeared to convert all of the Hg^0 to Hg^{2+} for the Comanche coal. For the Blacksville coal, the IAC provided 75% mercury removal at 250°F but only 15% removal at 350°F. For all three coals, the IAC injection resulted in almost no Hg^0 at the baghouse outlet.

The LAC provided over 80% mercury removal at temperatures of 250°F or less for all three coals, but at 300°F, vapor-phase removal was 70%, 50%, and 0% for Comanche, Absaloka, and Blacksville coals, respectively. From these results, we can conclude that the LAC effectiveness is highly dependent on temperature and coal type.

ESP Tests and COHPAC/TOXECON Tests

Very limited testing was conducted with the pilot-scale electrostatic precipitator (ESP) alone. The tests in general indicate that it will be more difficult to achieve high mercury removals with the ESP than with a baghouse. For the compact hybrid particulate collector (COHPAC) configuration, the results indicate that mercury removal is somewhat lower than for the same sorbent tested with a pulse-jet baghouse. However, the results are for one coal and sorbent and should not be generalized.

Other Trace Elements

Except for mercury and selenium, the results indicate that trace element removal is in general predicted by baghouse particulate removal. When the particulate removal was greater than 99%, removal of As, Pb, Cr, and Ni was also greater than 99%. Many of the measurements indicated that Cd removal was significantly less than 99%, but the Cd levels were near detection limits. Se removals were in all cases significantly less than the overall particulate removal, ranging from 61% to 97%, indicating that a fraction of the Se remains in vapor form at the exit of the baghouse.

Bench-Scale Injection Tests

Results from these tests were in general quite variable and not a source of definitive information. Several effects made interpretation of the results difficult. The sorbent was premixed with fly ash to facilitate feeding a very small amount of sorbent, but the fly ash itself was found to either collect additional mercury or convert Hg^0 to Hg^{2+}. Therefore fly ash effects could not be readily distinguished from sorbent effects. Some of the injected ash and sorbent mixture collected on the walls of the filter holder rather than on the filter alone. This made it difficult to determine exactly how much sorbent was exposed directly to the simulated flue gas. The Ryton® fabric itself was capable of reducing the mercuric chloride ($HgCl_2$) to Hg^0, making it impossible to test Hg^{2+}. No conversion was observed with the GORE-TEX® fabric, but the injection problems and fly ash effects remained. Therefore, this experimental approach is not recommended for further testing.

Results from the fixed-bed tests provided repeatable data on the capacity of IAC and LAC for both Hg^0 and $HgCl_2$ for several temperatures and sorbent concentrations. One of the important observations from the LAC tests is the initial sorption of Hg^0 followed by conversion and desorption. This indicates that the interaction of the sorbent, mercury, and other gas components is complex. While the fixed-bed tests can provide repeatable results and indicate relative capacity, temperature effects, and flue gas effects, the mechanisms are not well known.

Bench-Scale Residence Time Tests

Only very preliminary tests were conducted with this system, but initial results indicate it is not a useful approach to determine residence time effects.

Task 18 – Coal Ash Resources Research Consortium Research

The Coal Ash Resources Research Consortium (CARRC, pronounced “cars”) is the core coal combustion byproduct (CCB) research group at the EERC. CARRC focuses on performing fundamental and applied scientific and engineering research emphasizing the environmentally safe, economical use of CCBs. This consortium of member organizations, scientists, and engineers has a history of 10 years of addressing issues related to CCB utilization and disposal. CARRC member organizations, which include utilities and marketers, are key to developing industry-driven research in the area of CCB utilization and ensuring its successful application. The EERC team approach is emphasized in every aspect of the research effort. CARRC continued the partnership of industry partners, university researchers, and DOE addressing needs in the CCB industry through technical research and development projects. Technology transfer also continued through distribution and presentation of the results of research activities to appropriate audiences, with emphasis on reaching government agency representatives and end users of CCBs. DOE is a partner in CARRC through the EERC JSRP, which provides matching funds for industrial member contributions and facilitates an increased level of effort in CARRC. The final report for 1993–1998 was submitted in October 1998.

CARRC partners have evolved technically and have jointly developed an understanding of the layers of social, regulatory, legal, and competition issues that impact the success of CCB utilization as applies to the CCB industry in general and to individual companies. CARRC researchers and members feel confident in their ability to answer technical questions about CCB utilization that may be posed by potential users, regulators, and environmentalists. Technical research on CCBs is successful when it adds to the CCB information pool. Many CARRC tasks are designed to provide information on CCB performance, including environmental performance, engineering performance, favorable economics, and improved life cycle of products and projects. CARRC technical research tasks are developed based on member input and prioritization.

CARRC activities from 1993 to 1998 included a variety of research tasks, with primary work performed in laboratory tasks developed to answer specific questions or evaluate important fundamental properties of CCBs. The tasks summarized in the final report are 1) The Demonstration of CCB Use in Small Construction Projects, 2) Application of CCSEM for Coal Combustion Byproduct Characterization, 3) Development of a Procedure to Determine Heat of Hydration for Coal Combustion Byproducts, 4) Investigation of the Behavior of High-Calcium Coal Combustion Byproducts, 5) Development of an Environmentally Appropriate Leaching Procedure for Coal Combustion Byproducts, 6) Set Time of Fly Ash Concrete, 7) Coal Ash Properties Database (CAPD), 8) Development of a Method for Determination of Radon Hazard in CCBs, 9) Development of Standards and Specifications, 10) Assessment of Fly Ash Variability, and 11) Development of a CCB Utilization Workshop.

CARRC topical reports were prepared on several completed tasks: *Comparison of State Department of Transportation Specifications for Coal Ash Utilization*, *Sulfate Resistance of Fly Ash Concrete: An Overview of Selected Publications*, and *Scaling Resistance of Portland Cement Concrete Containing High Levels of Coal Combustion Fly Ash*.

CARRC research activities were enhanced by a variety of complementary activities, including CCB research projects funded from several different sources. Several of these projects were performed in an effort to allow members and nonmembers to fund small research projects through CARRC. These projects are jointly funded by the DOE JSRP at the EERC and are selected to provide information valuable to the CARRC research group. CARRC researchers' participation in activities of the American Coal Ash Association (ACAA), the American Society for Testing and Materials, and the Region 8 Ash Utilization Group also enhanced the CARRC research and allowed the results to be used more readily by the CCB industry. CARRC researchers participated in numerous regional, national, and international conferences and symposia as part of the ongoing effort to communicate with CCB producers, marketers, and end users. CARRC participation included presentations and developing and chairing conference series and sessions. CARRC researchers promoted CCB utilization through example by encouraging its use in University of North Dakota projects and even personal construction projects. These projects allowed CARRC researchers to work directly with end users of CCBs and develop a better understanding of their concerns.

In 1993, CARRC researchers also prepared a report for DOE titled *Barriers to the Increased Utilization of Coal Combustion/Desulfurization Byproducts by Governmental and Commercial Sectors*, facilitating DOE's preparation of a Report to Congress on barriers to CCB utilization which was important to the CCB industry. That report was updated in 1998 and submitted for publication by DOE. While the preparation of these reports was a separate effort from CARRC, the CARRC members were instrumental in providing vital information for the two reports.

The primary goal of CARRC is to work with industry to solve CCB-related problems and promote the environmentally safe, technically sound, and economical utilization and disposal of these highly complex materials. Individual goals are set on an annual basis, and CARRC researchers have successfully achieved the majority of annual technical and technology transfer goals with contributions of materials, technical guidance, and information on industry perspective from CARRC members.

CARRC 1993–1998 accomplishments included:

- Updating the CAPD to a user-friendly database management system and distributing it to CARRC members.

- ASTM standard preparation for a guide to using CCBs as waste stabilization agents.

- Preliminary identification of specific mineral transformations resulting from fly ash hydration.

- Limited determination of the effects of fly ash on the set time of concrete.

- Statistical evaluation of a select set of fly ashes from several regional coal-fired power plants.

- Development and presentation of a workshop on CCB utilization focused on government agency representatives and interested parties with limited CCB utilization experience.

- Participation in a variety of local, national, and international technical meetings, symposia, and conferences by presenting and publishing CCB-related papers.

Task 19 – The Application of FBC Residues for High-Volume Utilization Options

The commercial sponsor withdrew from this project before work commenced, and the allocated DOE–EERC JSRP funds were not expended.

Task 20 – FT-IR Spectroscopic Investigation of Fireside Deposit in a Pilot Plant Combustor

Successful operation of conventional, as well as advanced, coal combustion systems depends on controlling and minimizing the development of ash fouling and slagging, i.e., fireside deposits. The development of these deposits depends not only on combustion design and operating conditions, but also on the composition and quantity of inorganic species in the coal. The increasing demand for control and mitigation of ash deposition in combustion boilers necessitates refined and advanced technologies. As a means of optimizing the control strategy, a distinct need exists to obtain improved and faster identification of imminent ash deposition. New advanced spectroscopic techniques offer the potential to achieve this goal.

An accessory for an FT-IR spectrometer was designed to monitor deposit formation in the convective pass of a pilot-scale combustor. This accessory, an IESP, provides a means to monitor infrared emissions produced inside the furnace duct. The probe is designed to fit into a standard optical access while still providing operator viewing through the port.

Tests involving the collection of emission spectra of ash deposits on the furnace duct and deposition probes under coal-fired operating conditions of the combustor were conducted on two coals using the IESP probe. The IR monitoring of ash deposits was evaluated using Antelope subbituminous and Illinois No. 6 bituminous coals.

Data collected using the IESP indicate that the current instrument configuration offers promise for application as a deposit thickness monitor. No information could be obtained on deposit chemistry during formation using this configuration of the IESP; however, several improvements in the instrument can be made that will make it more effective in the measurement of deposit chemistry.

The capability of FT-IR for remotely monitoring deposit thickness has been demonstrated. After some refinement of the optical interface and development of turnkey software, further investigation of the infrared emissions of ash deposits can be done. The development of the FT-IR technique coupled with the IESP can be continued to advance the capabilities for determining deposit chemistries in situ. In addition, for the application of remote IR measurements to deposit thickness, a simple optical instrument can be developed using the concept of a two-wavelength measurement. The new instrument will be much less complicated to construct and operate than an FT-IR spectrometer and may be a hand-held device similar to an optical pyrometer.

The final report for this project was submitted in December 1995.

Task 21 – Sour Gas Plant Remediation Technology Research and Demonstration Project

During the period from 1993 to 1996, a long-term program was initiated to conduct remediation research at the Strachan Gas Plant in Alberta, Canada. As part of this research program, optimization of the existing pump-and-treat facility was of interest. The cost-effective treatment of contaminated groundwater produced from the pump-and-treat system was complicated by several factors, including 1) increased cost and reduced effectiveness of most water treatment processes because of the cold temperatures and severe winter conditions prevalent in Alberta, 2) interference caused by the mixture of inorganic and organic contaminants found in the groundwater that can reduce the effectiveness of many water treatment processes, and 3) pretreatment to prevent scaling in existing treatment process unit operations caused by the iron, manganese, and hardness of the contaminated groundwater.

The development and evaluation of two groundwater treatment processes were initiated during the project period, both of which use freeze crystallization for remediation of contamination. This research, sponsored by the Canadian Association of Petroleum Producers (CAPP) and the DOE, was conducted by the Resource Technology Corporation (RTC, now B.C. Technologies) of Laramie, Wyoming, under a subcontract from the EERC. The final report for the project was submitted in April 1997.

One of the processes developed and evaluated for remediation of contaminated water associated with sour gas production and processing uses artificial refrigeration to freeze and, subsequently, purify the water. This process is similar to commercially available freeze crystallization water purification processes successfully in use in both the United States and Canada. The design of this unit has the potential to reduce both unit size and capital equipment requirements relative to those of existing commercial units. The second process under development during the project was a natural freeze–thaw process. This process utilizes naturally occurring atmospheric conditions to generate usable water from contaminated groundwater during the winter months.

A prototype of the RTC–EERC artificial freeze crystallization process was constructed, extensively shaken down, and modified. A series of ten experiments was conducted to begin the optimization of the artificial freeze crystallization process prototype. The study of the natural freeze–thaw process consisted of several steps, including review of chemical analyses from the Strachan plant contaminated groundwater; evaluation of the regulatory climate in Alberta, Canada; obtaining and compiling meteorological data for Rocky Mountain House, Alberta, Canada, to produce monthly estimates of daily average temperature cycles for use in the laboratory-scale natural freeze crystallization simulator; and performance of a 21-day simulation of the natural freeze crystallization process using samples of contaminated groundwater from the Strachan Plant.

Although the operation of the artificial freeze crystallization process prototype was not optimized for the treatment of contaminated groundwater, the process was shown to be capable of removing significant quantities of contaminants from the groundwater. The prototype successfully reduced the electrical conductivity (EC) of groundwater by 62% and increased the EC of the brine generated by 52% compared to the contaminated feed. Modifications that should be made to improve the operability and efficiency of the prototype include increasing the operating pressure of the feed in the refrigerant evaporator heat exchanger, increasing the maximum centrifuge speed, improving the performance of the ice scraper and ice removal system for the prototype’s centrifuge, and adding another air–liquid refrigerant evaporator to the centrifuge housing. If we assume that the prototype modifications result in the expected improvements in efficiency, the potential for commercial use of the process is promising. It appears that it would be prudent to continue to invest in the development of the artificial freeze crystallization process.

Since the start of this project, the natural freeze–thaw process has been demonstrated on a commercial scale in New Mexico. The natural freeze crystallization process appears to be suitable for use in treating contaminated groundwater from the Strachan Plant. Both the size of the Alberta, Canada, gas industry and the favorable climate for freezing imply that it would be beneficial to test the natural freeze–thaw process and apply the technology to the treatment of the natural gas industry's groundwater.

Additional laboratory-scale simulations should be conducted to provide supplementary information regarding the behavior of organic compounds. The use of the natural freeze crystallization process should be demonstrated at the Strachan Plant during a field test.

Task 22 – Evaluation of Supercritical Fluid Extraction (SFE) for Analysis of Petroleum Industry Waste

This project, sponsored by the American Petroleum Institute and DOE with additional assistance from EPA, was designed to evaluate and improve SFE methods and instrumentation for the analytical-scale extraction of petroleum hydrocarbons ranging from benzene, toluene, ethylbenzene, and xylene (BTEX) components to polycyclic aromatic hydrocarbons (PAHs) and heavy crudes from soils and sludges. The evaluation included the use of "standard" SFE approaches (such as the proposed EPA method for total petroleum hydrocarbons [TPH]) and commercially available instrumentation with comparisons to standard liquid solvent extraction methods. A final report was submitted in the fall of 1994.

Good comparability for TPH (gasoline and diesel range) was demonstrated between conventional Soxhlet extraction and SFE using conditions similar to the proposed EPA SFE method (using both IR and GC–FID quantitation of the extracted hydrocarbons), although SFE yielded higher efficiencies for the more volatile (e.g., BTEX and related alkanes) components because of lower extraction losses than Soxhlet extraction. The use of SFE in the field also gave good agreement for TPH using IR determination for gasoline and diesel-range organics compared to SFE and conventional Soxhlet extractions performed in the lab. Commercial instruments using both solvent trapping (ISCO) and sorbent trapping (Hewlett-Packard) yielded quantitative recoveries (>90%) of BTEX and gasoline- and diesel-range alkanes as volatile as C6 (for sorbent) and C7 (for solvent trapping), demonstrating that BTEX and TPH determinations can be performed with a single extraction.

An on-line SFE–GC method for gasoline- and diesel-range organics was also developed that allows species as volatile as *n*-butane to be extracted and collected at about 100% efficiency. In addition to allowing quantitative determinations of very volatile species, the SFE–GC method allows sensitive detection limits (e.g., <10 ppb for benzene) for samples as small as 1 gram. However, the on-line method is more difficult to perform than the standard SFE methods and requires modifications to existing SFE and GC instruments.

SFE methods were also developed utilizing high-temperature SFE and the addition of organic modifiers for components that were not efficiently extracted using standard SFE conditions (e.g., heavy hydrocarbons and PAHs). With the combined use of either high SFE temperatures (e.g., 150 °C) and/or organic modifiers, the recoveries of heavy hydrocarbons (e.g., heavy resids >C40) were higher than those achieved using Freon-113 Soxhlet extraction (as determined by IR). In general, contaminated soils could be extracted as-received (i.e., no drying or any other pre-preparation), although samples contaminated with high levels of heavy hydrocarbons (either soils or waste sludges) often caused plugging of some types of SFE flow restrictors. In nearly every case, heating the restrictor and mixing such samples with dispersants and/or drying agents eliminated restrictor plugging.

Practical advantages of SFE included extraction times of typically 30–40 minutes (compared to 4 hours or greater for Soxhlet extraction) and total solvent use generally <10 mL (compared to 150 mL for Soxhlet extraction). In nearly all of the samples studied, SFE yielded efficiencies similar to or higher than Soxhlet extraction; however, elevated temperature and/or organic modifiers were often needed to obtain high extraction efficiencies for organics larger than gasoline and diesel range. It should be noted that SFE instruments continue to evolve, especially in the areas of improved restrictor and collection system designs as well as systems offering automated extraction of up to about 20 samples without operator intervention. Such developments should further increase reliability and speed of SFE for petroleum hydrocarbon extractions from soils and sludges.

Task 23 – Gas Industry Groundwater Research Program

Alkanolamine- and glycol-related subsurface contamination issues have in recent years become the focus of some environmental concern. In 1996, EERC efforts in the Gas Industry Groundwater Research Program, sponsored by DOE and GRI focused research activities on evaluating the nature and subsurface transport and fate of alkanolamine- and glycol-related contamination at natural gas-processing sites.

The objective of this project was to provide the natural gas industry with data and insights regarding the chemical nature of gas-sweetening and dehydration wastes and the natural attenuation processes that control the subsurface transport and fate of the alkanolamines and glycols and their associated wastes. Such information will enable the natural gas industry to 1) significantly improve the assessment of subsurface alkanolamine and glycol-related contamination at sites where it is known or suspected to occur and 2) make sound decisions concerning the remediation of that contamination and the management of related wastes.

The systematic series of laboratory-based research activities focused on the subsurface transport and fate of amine- and glycol-related wastes to determine the potential environmental hazards that those wastes may pose. A three-pronged approach included 1) organic and inorganic waste characterization, 2) determination of contaminant interactions with soils and water, and 3) evaluation of the biodegradability of amines and their associated wastes. DEA and MDEA and wastes generated by gas-sweetening units that utilize those alkanolamines were the focus of the amine-related studies. Glycol research has focused on subsurface issues related to triethylene glycol (TEG) and ethylene glycol (EG). TEG was selected for examination because it is used in a vast majority of gas dehydration units, and EG was chosen because it is currently under regulatory scrutiny as a drinking water pollutant.

Amine Waste Characterization, Interaction, and Biodegradability

Samples of waste material from twelve amine-based acid gas removal (AGR) units at eight gas-sweetening facilities in Texas, Louisiana, and Alberta (Canada) representing a broad range of gas compositions were obtained. These included spent DEA and MDEA liquid solutions from six different sweetening units, sludges from reclaimer units, and filters from three different DEA-based sweetening units. The twelve samples of amine-derived waste material were analyzed by gas chromatography coupled with mass spectrometry (GC–MS), GC–AED, GC–FID, capillary electrophoresis (CE) and ion chromatography (IC). The analysis of DEA and MDEA wastes recovered from AGR treatment units, filters, and a reclaimer unit indicated that sludges are significantly more complex in composition than spent AGR liquid solutions, which contain primarily parent amine and water.

A key parameter in describing the interaction of any compound with sediment and water is its aqueous-phase sediment distribution coefficient (K_d), which quantitates the partitioning of a compound between the aqueous and adsorbed states, thus indicating its potential for mobility. Uncontaminated base sediments from three gas-producing regions of North America were collected for performance of laboratory tests to determine K_d values for DEA and MDEA. The data show that DEA and MDEA are both adsorbed significantly on typical sediments and are relatively immobile. These amines range in mobility from low to intermediate.

The biodegradabilities of three DEA sludges were evaluated in aqueous slurries of soil. It was concluded that contamination of soils with DEA should be rapidly mitigated in soils such as those found in New Mexico and Alberta, provided sufficient water and oxygen are present, that temperatures are conducive, and that the concentration of DEA is not so elevated as to be toxic. However, the biodegradation of DEA-related sludges is much different from treatment of DEA in soils. These sludges contain a wide variety of compounds, some of which are toxic or inhibitory and others for which microbes that have the ability to biodegrade them may be rare. The experiments conducted thus far on the biodegradation of DEA sludges in the three soils in aqueous slurries showed that a significant fraction of the material is biodegradable under slurry bioreactor conditions. However, after biodegradation is stopped, a significant amount of material remains that is recalcitrant to biodegradation. It is clear that the biodegradation of amine sludges represents a very different problem from that of biodegradation of the parent amine.

Glycol Waste Characterization and Biodegradability

Identification and semiquantitation of organic cocontaminants in glycol-related dehydration wastes were performed using organic solvent extracts and solid-phase microextraction (SPME) extracts that were characterized using GC–MS, GC–AED, and GC–FID. The presence and abundance of organic cocontaminants in lean glycol solutions was found to vary widely from facility to facility. In fact, at some facilities it was difficult to differentiate between lean and rich samples based on the analytical results alone. Other notable observations that resulted from the characterization activities include the lack of significant levels of chlorine- and bromine-containing organics and the presence of significant organosulfur compounds in the rich EG sample.

Biodegradation testing was conducted to evaluate the length of the acclimation phase, the rate constant for biodegradation, and the extent of biodegradation under aerobic conditions for TEG in soils collected from natural gas-producing regions of New Mexico, Louisiana, and Alberta, Canada. The fastest biodegradation rates were observed in the Alberta sediment at both a low and a high dose. Biodegradation of TEG in the New Mexico sediment was similar to Alberta in rate, extent, and length of the lag period at the low dose, but this sediment was only poorly biodegraded at the higher dose. Biodegradation of TEG in the Louisiana sediment was poor for both the low and the high dose. The rate of anaerobic TEG biodegradation in Alberta sediment was 27% of that found at the same dose under aerobic conditions. Anaerobic biodegradation of TEG in the Louisiana and New Mexico sediments was much slower than for the Alberta.

The results of the characterization investigations have demonstrated that a range of organic cocontaminants (e.g., BTEX, PAHs, alkanes, and other process-related organic cocontaminants) is associated with glycols used for natural gas dehydration, particularly “rich” glycols. Future investigations of the subsurface environmental effects of dehydration glycols will be designed to determine the effect of glycols on the transport of organic cocontaminants.

Another lesson that stands out from the results of the research is that site-specific variables need to be considered in assessing glycol-related contamination in the subsurface. For instance, the results of the biodegradability evaluations, which consistently show biodegradation to be inhibited in the Louisiana soil, suggest that soil type may be an important factor in predicting the ultimate fate of TEG in the subsurface environment.

Overall, the waste characterization results show the greatest degree of variability in the composition of amine-associated wastes, especially sludges and indicate the need for more characterization and quantitation of waste components other than the amines. Such variability in sludge composition, coupled with significant differences in amine behavior between different soil types, indicates that predicting the impact of amine-related wastes on any given subsurface environment largely depends on site-specific conditions. It is important to note that soil conditions within a region can vary substantially, and, therefore, site-specific soil characterization data (particularly pH, total organic carbon, and cation exchange capacity), along with knowledge of cocontaminants that may be associated with the alkanolamines (i.e., presence of additives and/or T/O reaction products), are essential to predicting the behavior of alkanolamines at any particular site. The presence of significant amounts of nonoxynol, PAH compounds, benzene and its derivatives, and T/O products suggests that the amines themselves may not be of primary concern from a risk management perspective. Instead, many of the compounds that are added to the solution, either intentionally or unintentionally, and compounds generated during the sweetening process may be of more concern from a toxicological and regulatory standpoint than the amines.

Task 24 – Pilot Plant Assessment of Blend Properties

The 1990 CAAA called for reductions in emissions of sulfur dioxide, with a limit set at 0.52 kg of SO_2/GJ (1.2 lb of SO_2/MMBtu) by the year 2000. Among the many control strategies available, coal blending and switching have received wide consideration. To aid the utility industry in these transition years, EPRI and DOE have provided funding for research efforts aimed at determining the effects of firing subbituminous coals in boilers designed for bituminous coal. A final report was submitted in December 1997.

Coal blending and switching have become increasingly common among utilities firing high-sulfur bituminous coals as they strive to meet regulated SO_2 emissions standards. Limited availability of low-sulfur bituminous coal and low market prices have created an increasing demand for low-sulfur subbituminous coals. However, these coals are very different in composition from the bituminous coal supply and have an effect on many operating characteristics when fired in boilers designed for bituminous coal. A pilot-scale study was conducted at the EERC to determine the relative impacts of a subbituminous coal or blend containing subbituminous coal on unit operating characteristics such as mill performance, furnace wall slagging, convective pass fouling, and electrostatic precipitator performance.
Mill performance tests were performed by CONSOL, Inc., at its facility in Library, Pennsylvania, while all other testing was performed at the EERC in Grand Forks, North Dakota.

Mill performance tests indicated that at design pulverizer conditions (relative to pulverization of bituminous coal), the decreased thermal input of the subbituminous coals resulted in derates on the mill of up to 55% of the maximum thermal input of the bituminous coals. One Pittsburgh seam bituminous coal, one Illinois No. 6 seam bituminous coal, and two PRB subbituminous coals were tested. Raising the mill outlet temperature between 3° and 14°C (5° and 25°F) allowed thermal throughput for the subbituminous coals to be increased by 10% to 20%. Increasing the air:fuel ratio also tended to increase thermal throughput, but at the expense of a coarser product. At the maximum thermal throughput for the subbituminous coals and at the highest air:fuel ratio, product fineness (less than 75 µm [200 mesh]) decreased by up to 15 percentage points. Interestingly, the lowest-heat-content subbituminous coal exhibited the lowest thermal derate of the two PRB coals tested, but required much higher mill energy input.

The effects of blending one Pittsburgh seam bituminous coal with two PRB subbituminous coals were tested. The tests were to determine the propensity for fouling of high-temperature heat-exchange surfaces exposed to high flue gas temperatures (both 1100° and 1200°C [2000° and 2200°F]), the propensity for fouling of low-temperature heat-exchange surfaces exposed to moderate flue gas temperatures (815° to 870°C [1500° to 1600°F]), flame stability characteristics, and gaseous and particulate emission characteristics. High-temperature fouling tests indicated comparable fouling rates for each of the parent coals, with the blends exhibiting a lower ash-fouling rate. This was attributed to interactions between the two ash types. However, in each case, the strength of the deposit increased irrespective of the fouling rate as the percentage of subbituminous coal in the blend was increased. The highest-sodium-content subbituminous coal produced consistently stronger deposits than its lower-sodium counterpart.

Low-temperature fouling tests indicated that similar deposition rates could be expected for each of the fuels tested, with a slight increase in rate noted as the percentage of subbituminous coal in the blend was increased. It was expected that as the percentage of subbituminous coal in the test fuels increased, with corresponding increases in fuel ash calcium concentrations, the resulting low-temperature deposits would develop increasingly greater strengths because of the effect of ash calcium content on deposit sintering behavior. Results were inconclusive to support this theory, as the parent coals exhibited much lower strength than any of the blends tested. There would appear to be some interaction between ash types to create the stronger deposits, although the mechanism was not easily discernible from the data generated.

Flame stability testing indicated that each of the parent coals and coal blends would exhibit excellent fuel ignitability and flame stability characteristics over a wide range of burner settings. There was a general trend toward lower carbon-in-ash values as the percentage of subbituminous coal in blend with the bituminous coal was increased. On the basis of results obtained here, the use of subbituminous coal in blend with the bituminous coal should increase overall carbon conversion and provide adequate or improved flame stability, which could offset some of the limits to grinding efficiency noted above in the mill performance tests performed by CONSOL.

Flue gas emissions of SO_2 were dramatically reduced as the percentage of subbituminous coal was increased in blend with the bituminous coal tested here. In general, the emission reductions corresponded to decreases in the input sulfur concentrations. However, there was evidence of increased sulfur capture in the ash as the percentage of subbituminous coal in the blends increased. This trend was even more pronounced for those tests performed at the lowest furnace exit gas temperature, indicating a temperature dependence on the level of sulfur capture in ash. Emissions of nitrogen oxides (NO_x) also decreased as the percentage of subbituminous coal in the blends increased. Levels noted during testing of the parent subbituminous coals were roughly one-half that of the parent bituminous coal.

Particulate emission testing indicated similar results for all fuels tested under similar conditions. There was no apparent trend toward decreased collection efficiency via electrostatic precipitation for either of the bituminous/subbituminous coal blend sets, although one of the blend sets indicated a slight reduction in collection efficiency as the percentage of subbituminous coal in the blend increased.

Relative to the baseline bituminous coal, the testing reported here indicated that there were significant impacts to boiler performance due to the blending of the eastern and western coals. Results indicated that fuel blending can be used to adequately control flue gas emissions of both SO_2 and NO_x at the expense of reduced milling efficiency, increased sootblowing in the high-temperature and low-temperature regions of the boiler, and to a lesser extent, decreased collection efficiency for an electrostatic precipitator. The higher reactivity of the subbituminous coal increased the overall combustion efficiency, which may tend to decrease the impact of milling efficiency losses. The extent of these impacts was directly related to the percentage of subbituminous coal in the blends. At the lowest blend ratios of subbituminous coal, the impacts were greatly reduced.

Task 25 – Physical Cleaning of Lignite

The goal of this project done in partnership with DOE, the North Dakota Industrial Commission, and the Knife River Coal Mining Company was to produce cleaner fuel from lignite (lower sulfur, ash, and sodium contents and higher Btu) in approximately 1-in. lumps using physical cleaning, briquetting, and drying methods. The goal of this phase was to determine the best initial conditions under which to produce a specification product. A final report on this work was submitted in September 1994.

A large quantity (about 1500 lb) of run-of-mine lignite from the Beulah Mine has been successfully pulverized, screened, physically cleaned, briquetted (about 300 lb), dried, and treated at the EERC to produce a product that meets sulfur emission requirements and represents a higher heating value product. Even though none of the processing steps have been optimized, high yields of about 80% were achieved. With optimization, these should approach 92%. The lignite was physically cleaned from about 1.2 wt% sulfur based on a moisture-free (mf) coal basis and 9.5 wt% ash mf to as low as 0.5 wt% sulfur mf and 6.1 wt% ash mf. Sodium content of the ash was 4.5 wt%, determined as sodium oxide. Locally available binders (feed wheat [4 wt%] and waste newspaper [3 wt%]) were investigated and found to produce briquettes with compressive strength values of 50 psi even after soaking in water. Surface spray treatment with oil or emulsified asphalt at a rate of 0.5–1 wt% per ton of briquettes was found to help preserve strength during soaking in water. Equilibrium moisture values were about 18–20 wt%, with none of the binder concentrations and surface treatment methods optimized.

Prior float–sink and water classification tests with Gascoyne lignite indicated that while a considerable amount of sulfur and ash could be removed by physical cleaning, a sulfur compliance fuel was not produced. A preliminary test indicated that the Beulah Mine lignite could be physically cleaned to produce a compliance fuel. The work was then changed to focus on the use of Beulah Mine coal, with excellent results.

Task 26 – Remote-Site Power Generation Opportunities for Alaska

The Alaska Native, American Indian, and Native Hawaiian Remote-Site Power Generation Workshop: Transferring the Alaskan Experience built upon the Small Alternative Power Generation Workshop held in Anchorage, Alaska, in May 1994. Under Alaska Division of Energy (ADE) and DOE sponsorship, Alaska Natives, state officials, and representatives from industry, universities, and DOE discussed the energy needs of the indigenous villages and identified the most suitable energy options to meet those needs. Since that time, projects have progressed to demonstrate these small, easy-to-operate-and-maintain, environmentally friendly, economically acceptable technologies using indigenous fuels and waste materials to produce electricity and heat. This format was used to transfer the lessons learned to date in Alaska to Native Hawaiian and American Indian communities throughout the United States. The overall objectives of the workshop were to share the results of activities undertaken to meet the energy needs of remote villages in Alaska and to explore the opportunities that exist to commercialize the technologies and transfer-related information to other indigenous communities.

The second workshop, held on September 25–26, 1995, in Seattle, Washington, with DOE–EERC Base Cooperative Agreement funding was attended by over 40 individuals representing a diverse group including Alaskan Natives, American Indians, Native Hawaiians, equipment vendors, resource developers, and technology developers.

An overview of those technologies currently being considered for initial demonstration projects was presented, including FBC coupled with either a steam or hot-air gas turbine, fuel cells, and a variety of renewable energy options. The technologies were ranked against a set of criteria developed during the 1994 workshop from needs of the Alaskan community. For the nonrenewable options, fuel availability is an issue, since no coal mines or gas wells exist there. Siting and cost are the main barriers to renewable energy sources. Based on the technical evaluation performed, FBC is the best solid fuel option for remote power generation, while fuel cells offer the best potential for utilizing natural gas or coalbed methane. These technologies are recommended for demonstration. Ongoing studies are evaluating the cost of implementing these technologies in several communities in Alaska.

This workshop was part of a larger Remote-Site Power Development and Demonstration project. The end goal was demonstration of remote-site power options in Alaska. Work has begun to progress toward that end through the activities of the various groups in Alaska with assistance from DOE. The EERC has provided assistance to these groups to catalyze the demonstration efforts.

Task 27 – Alaskan Low-Rank Coal–Water Fuel Environmental Attributes and Combustion Test Marketing

This work was jointly sponsored research between DOE and the Alaska Division of Energy (ADE) as a means to expedite a project to demonstrate at a commercial scale the production and utilization of coal–water fuel (CWF) made from hot-water-dried Alaskan subbituminous coal. Its objectives included developing low-rank coal–water fuel (LRCWF) combustion test programs with selected potential end users, defining the environmental benefits of replacing heavy oil with CWF, and updating the market video prepared with the Alaska Energy Authority, now the Division of Energy.

A one-page brochure describing in nontechnical terms LRCWF production, utilization, its environmental attributes, its potential role in opening the Beluga coal field, and the proposed demonstration project was prepared, and over 1500 copies have been distributed. It was well received, especially by members of the Alaskan legislature, and proved invaluable in developing broad-based support for the demonstration project in the Alaskan state legislature.

An approximately 10-minute video following the script for the brochure was prepared by Mind's I Productions. The new video is an update of the original LRCWF video produced by the former Alaska Energy Authority. The new video presents hot-water drying, LRCWF production, , utilization, and the environmental attributes of LRCWF in nontechnical terms through the use of live shots and cartoon animation.

The following is a summary of all of the work completed under Phase I of the Alaska LRCWF Demonstration Project. The two key subtasks funded by the ADE–DOE–EERC joint venture agreement were Subtasks 2.2 and 3.3, End-User Testing Agreements, and Subtask 4.2, Environmental Attributes of LRCWF. In addition, this funding made possible the creation of the Alaskan LRCWF brochure and video.

In June 1994, Alaska Science and Technology Foundation (ASTF) provided $185,000 to the Alaska Industrial Development and Export Authority (AIDEA) (ASTF Grant Agreement No. 91-3-189). AIDEA was to serve as grant administrator for Phase I of the Alaska LRCWF Demonstration Project. This funding was to be matched by $244,000 of in-kind contribution by participating members of the LRCWF Consortium, which during the course of Phase 1, became Alaska Coal–Water Fuel (ACWF). A summary list of accomplishments follows:

- Articles of Consortium Incorporation. ACWF was formed in June 1994 between Usibelli Coal Mine, Inc., and the EERC Foundation to be the legal entity representing the former LRCWF Consortium.

- Joint Venture Agreement. A joint venture agreement between AIDEA and ACWF for Phase 2 of the demonstration project was constructed from the Memorandum of Understanding for Phase 1.

- Prefeasibility Business Plan. The prefeasibility business plan developed (by DRven) provides a brief description, price, strengths and/or weaknesses of competing fuels and technologies and an initial strategy for competing in the target markets.

- Market Potential and LRCWF Costs. Despite having energy policy plans aimed at decreasing the use of oil in the utility sector, actual utility oil consumption increased in 1990–1992 by over 15%, the equivalent of 92 million tons of LRCWF annually in the North Pacific Basin. LRCWF production cost estimates suggest that LRCWF can be produced for prices within the window of opportunity for low-sulfur waxy residual as defined in the prefeasibility business plan.

- End-User Test Agreement. To date, the only written commitment to test LRCWF is by the University of Alaska–Fairbanks (UAF). UAF plans to test LRCWF in one of the oil-fired boilers and, if the test is successful, will examine phasing out oil use on campus entirely.

- Environmental Attributes of LRCWF and Permitting Initiation. Since LRCWF is simply coal dispersed in water, it is expected to be classified by federal and state environmental agencies as nonhazardous, like coal–water slurry. Power Engineers conducted a permitting study for each of the three sites under consideration for hosting the project and identified the permit requirements. Because of existing permits at the UAF power plant, it was determined that permitting time could be held to a minimum of about 6 months.

- Host Site Agreement. UAF is considered a leading candidate for host site and has provided a letter of agreement detailing their contributions. Their contributions include a building to house the production facility, all process heat and power, use of coal-handling equipment and an oil-fired boiler, and staff and faculty time. In total, these amount to over $4 million.

- Demonstration Project Design, Cost, and Cost Shares. LRCWF plant design, capital, and operating costs developed by EERC and ACWF were reviewed and modified by Power Engineers. Power Engineers considered the proposed cost of $21,023,000 conservative for the proposed 3-year demonstration using the base-case design.

- DOE Proposal. The DOE proposal outlines the requirements and merits for advancing the commercialization of a clean coal technology developed in the United States and production and utilization of LRCWF. Affiliates and principals of ACWF and ASTF through the AIDEA have committed approximately $6,973,000.

Task 28 – An Assessment of the Subsurface Fate of Monoethanolamine at Sour Gas-Processing Plants

In 1994, the EERC initiated a three-phase program to investigate the natural attenuation processes that control the subsurface transport and fate of MEA, the most commonly used alkanolamine in Canada. Funding for the MEA research program was provided by DOE, Canadian Association of Petroleum Producers (CAPP), Canadian Occidental Petroleum Ltd. (CanOxy), Environment Canada, and the National Energy Board of Canada.

Phase I Slurry Experiments

In 1994 and 1995, experimental activities were conducted at the EERC to evaluate the biodegradability of MEA sludge-contaminated soil in slurry bioreactors. The slurry experimental activities were designed to provide estimates of 1) the time required to initiate the biodegradation, 2) the rates of degradation of the contaminants, 3) the degree of difficulty in operation, and 4) the composition of the material remaining after slurry treatment.

Soil contaminated by MEA-related sludge biodegraded well for the first 15 days, but metabolism was slower thereafter. In general, the results of the Phase I bioslurry experiments suggest that land treatment of the MEA-contaminated soils may be a technically viable remediation technique.

Phase II Landfarming Experiments

Landfarming experiments conducted as part of Phase II were designed to examine the effectiveness of land treatment for reducing MEA-related contamination and toxicity in soil from the Okotoks, Alberta, site. The following key variables were evaluated: 1) phosphorus dose, 2) tillage frequency, 3) loading rate of contaminated soil, and 4) pH adjustment. Samples from the beginning and end of the study period were analyzed for toxicity, chemical oxygen demand, and total Kjeldahl nitrogen (TKN).

The results of the landfarm experiments showed that the most important variable affecting bioremediation was soil loading. The data showed that toxicity of some components in the contaminated soil resulted in reduced bioactivity, longer lag times, and reduced removals. Based on the bacterial luminescence test (Microtox®), toxicity in all landfarms at the lower soil loadings (10 and 17.5 wt%) was reduced to zero. However, the results of additional assessments via seed emergence, root elongation, and earthworm survival suggested that significant toxicity remains even in the lower soil-loading conditions. Further testing showed that the toxic fraction of the treated soil is extractable in both water and methanol, which suggests that those components may be leachable from the soil. The identity of these toxic components is not known.

Phase III Biopile Design and Operation

The water-soluble nature of the toxic components remaining in the contaminated soils indicates that they may be concentrated in leachate generated during bioremediation. On the basis of toxicity data, a system that is designed with a leachate collection system, such as an engineered biopile, may be a viable bioremediation technique.

In the spring of 1998, a demonstration-scale biopile operation was designed by the EERC and Hazco Environmental Services of Calgary. In the summer of 1998, Hazco constructed the biopile, and operation was initiated on August 5. Aeration, irrigation, and a leachate collection system define the dynamic components of the structure. Aeration is performed to supply oxygen to the microbial population, which, in turn, enhances biodegradation. Adequate soil moisture is also necessary to obtain appropriate microbial activity, although if the soil is saturated or nearly so, aeration will be inhibited. Therefore, water is periodically added to the biopile using an irrigation system. Leachate is collected by a sump unit housed directly below the crushed gravel layer and temporarily stored in a reinforced external tank (2000 imperial gallons).

Three thermocouples were placed inside the biopile to monitor temperature on a regular basis. Soil moisture was measured biweekly to determine the frequency of wetting. Samples of leachate generated during the operation of the biopile were scheduled to be collected after the first week of operation (August 1998), just prior to winter shutdown (late October 1998), after spring start-up (April 1999), and, finally, at the close of the field-based operations (June or July 1999). Toxicity tests will be conducted on samples of soil and leachate collected at the beginning and end of the biopile operation.

Laboratory results showing changes in the concentrations of amines and the T/O reaction products, as well as changes in toxicity, are pending. At this time, it is not possible to comment on changes in the toxicity of the soils or the composition of the leachate.

However, as of December 1, 1998, nitrogen-related data from several soil-sampling events were available. The TKN, ammonia nitrogen (NH_3-N), nitrogen oxides (NO_x-N), and total organic nitrogen (TON) results from one of the biopile plots show that TKN and TON are decreasing, while NH_3-N and NO_x-N are increasing with time. This general pattern would be expected if biodegradation of the nitrogenous organic compounds (i.e., amines and T/O reaction products) was occurring, since ammonia is produced as a result of the biodegradation of alkanolamines and other organic nitrogenous compounds and, eventually, may be oxidized to nitrate. Therefore, on the basis of nitrogen-related data from the 1998 operating season, it appears that the biopile operation is successfully removing a significant portion of the MEA-related contamination from the soil.

Aeration of the biopile was stopped on November 16, 1998. The biopile was remixed on November 27 to break up any channels that may have formed over the summer and fall. No sampling or monitoring activities are planned for the winter months. Reactivation of the aeration system and rewetting of the biopile are currently scheduled to begin in March 1999 and continue until June 1999.

Task 29 – Mitigation of Air Toxics from Lignite Generation Facilities

This project was formed to address possible forthcoming hazardous air pollutant (HAP) regulations and to evaluate trace element concentrations and possible mitigation methods for lignite generation facilities. The work performed under this project focused on characterizing emissions from five lignite coals from North Dakota—Beulah, Falkirk, Freedom, Center, and Gascoyne. A Montana Savage mine lignite and a PRB subbituminous coal from the Big Sky mine were included for comparison with the North Dakota coals. In addition, research activities were performed to identify and test control technologies that would mitigate HAP emissions. Specifically, the objectives of the project were twofold: 1) to determine the trace element concentrations of six lignite coals and one PRB coal, 2) to test the most promising trace element mitigation methods, and 3) to simulate the amount of trace element collected in bottom ash and by standard fly ash collection equipment such as baghouses and electrostatic precipitators.

The concentrations of eleven trace elements were determined for each coal evaluated. The coals were analyzed using state-of-the-art methods, including atomic absorption (AA) and inductively coupled argon plasma spectroscopy (ICAP), to determine the concentrations of antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cd), cobalt (Co), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), and selenium (Se).

To develop possible control technologies for these trace elements, precombustion and postcombustion sorbent injection, along with a gas-conditioning agent, were tested. In addition, because the alkali and alkaline-earth components (sodium, magnesium, calcium) in these coals may adsorb many of the trace elements of concern, the ash constituents were also considered as possible sorbents. The potential for these technologies to provide mitigation of trace element emissions was reviewed, and the most attractive techniques were chosen for testing.

The most promising precombustion sorbents were zeolite, kaolinite, and limestone; however, lime was also evaluated as requested by the project sponsors. These were selected for trace element emission mitigation along with a postcombustion sorbent, lignite-based activated carbon (LAC). Sulfur trioxide (SO_3) injection, as a flue gas-conditioning agent, was evaluated on a limited basis to determine its potential impact on trace element and particulate collection. Bench-scale (Phase I) tests were performed on Beulah coal in the EERC DTF. Pilot-scale (Phase II) testing of the sorbents and SO_3 conditioning agent were performed on Beulah, Falkirk, and Freedom lignites, and a PRB subbituminous (Big Sky) coal in the EERC particulate test combustor (PTC) to accumulate scaleup data on sorbent effectiveness.

Phase I of the project consisted of testing three precombustion sorbents—zeolite, kaolin, and lime—in a bench-scale, laminar flow DTF to determine their effectiveness in capturing the trace species. Both particulate and gas samples were obtained during the tests to determine their trace element contents. The three additives were blended with pulverized Beulah coal on a 10% by weight, coal ash basis. Lime was also blended on a 50% and 100% by weight, coal ash basis. The parent Beulah coal and coal additive blends were tested in the DTF using conditions typical of pulverized coal-fired boilers. Key results from the DTF test are summarized below:

- As and Ni were completely captured by the ash in all the DTF tests, indicating that sorbent addition is unnecessary for controlling the emission of As and Ni for the Beulah coal.

- Kaolin was determined to be unsuitable as a trace element sorbent because of its enrichment in Pb, Ni, Hg, and Se.

- The zeolite tested was ineffective in removing Pb, Hg, or Se vapors from flue gas.

- Lime was somewhat effective for controlling Hg and Se.

- Hg and Se control with lime addition is probably cost-prohibitive.

Phase II consisted of testing the selected precombustion sorbent (lime), the postcombustion sorbent (LAC), and the gas-conditioning agent (SO_3) in a pilot-scale, 161-kW (550,000-Btu/hr) PTC equipped with a baghouse. The mitigation tests were conducted with four of the seven previously analyzed coals based on feedback from the project sponsors. These were the Beulah, Falkirk, and Freedom lignites and Big Sky (PRB) subbituminous coals. Particulate and gas samples were collected and analyzed using currently accepted/modified EPA methods. A total of twelve runs were completed, consisting of the baseline, LAC injection, and lime runs for the Beulah, Freedom, and Big Sky coals and baseline, LAC, and SO_3 runs for the Falkirk lignite.

Key results from the PTC tests are summarized below.

- Injected LAC was the most successful of the sorbents tested on the three North Dakota lignites. The injection of the LAC sorbent dramatically decreased baghouse emissions of mercury in the three North Dakota lignite runs; mercury reductions were over 98%. The best results were with LAC injection during the Beulah and Freedom lignite combustion tests. These coals exhibited relatively high mercury volatility and emissions (8.71 and 7.15 $\mu g/m^3$, respectively) without the use of the LAC. Baghouse emissions of Hg in the Falkirk runs did show improvement over the already excellent baseline results for that coal. With the injection of LAC during the Big Sky test, mercury collection efficiency doubled from approximately 10% to 25%, but Hg emissions still remained relatively high (2.90 $\mu g/m^3$ compared to 0.23 $\mu g/m^3$ for the Beulah). The reason LAC appeared to be effective for the ND lignites and not the PRB subbituminous coal is not known at this time. Further parametric testing would be required to determine the conditions and/or factors that influence the sorption mechanisms. Mercury speciation is known to be a critical issue; however, proven methods (EPA reference standards, etc.) do not currently exist to properly speciate mercury. Additional testing will be required to determine optimum rates before economic assessments can be performed.

- Baseline run results indicate that the solid-phase trace elements, mainly As, Ni, and Pb, were captured relatively well by the baghouse for all coals tested. The addition of sorbents did appear to consistently improve their capture; however, the improvements were small in all but the subbituminous case and may not be statistically valid. The Big

Sky subbituminous combustion data did indicate decreased As and Pb emissions with LAC addition and decreased emissions in As, Pb, Ni, and Se with the use of the precombustion lime sorbent. The addition of lime appeared to enhance the collection of As and Se for both the ND lignites and the PRB. The lime also reduced sulfur dioxide (SO_2) emissions significantly, as expected. As with the LAC injection rates, the lime was added to the coal at a high rate (1.8–2.7 kg/45.4 kg [4–6 lb lime/100 lb] coal) to determine whether it would be effective. Based on these rates and the slight improvements observed, lime as an additive to the coal to control trace element emissions is not likely a cost-effective control strategy. Furthermore, additional disposal costs would also have to be considered. Although the addition of lime will assist in SO_2 reduction, the levels at which the trace elements (i.e., mercury) will be reduced is minimal and may not meet future regulatory standards.

- Evaluation of SO_3 flue gas conditioning (at 15–20 ppm) was performed on a very limited basis on one run with the Falkirk lignite. Unfortunately, the Falkirk was not a good test coal, since the baseline case exhibited good trace element reduction across the baghouse without the use of any additives/sorbents. Although it was speculated that it might enhance As and Se removal, based on the limited data generated, SO_3 injection appeared to have little or no impact on trace element emissions. As these conclusions are based on very limited and preliminary data, they should not be applied until further testing is conducted.

- Use of the precombustion lime sorbent in the PTC tests exhibited a distinct reduction in flue gas levels of SO_2 over the baseline and LAC combustion runs. The best examples of this are the Beulah and Freedom runs in which SO_2 emissions were reduced approximately 62% and 66%, respectively.

- The precombustion lime, LAC, and SO_3 flue gas conditioning appeared to have little or no effect on NO_x emissions.

- The injection of LAC did not appear to have any impact on Cl and F emissions. The addition of lime may have had a minimal effect on Cl emissions for the Big Sky coal and no effect on the ND lignites. Halogen data were limited, and further analyses should be conducted before any effects due to the use of sorbent technology are ruled out.

- The residues (ashes) tested from all runs were determined not to be hazardous on the basis of RCRA definition. On the basis of bulk ash and leachate characterization results, no additional disposal requirements would be anticipated beyond those already required at a given utility disposal site. The addition of lime or injection of LAC does not appear to cause any detrimental concentrations of hazardous elements in the fly ash. On the basis of short- and long-term leachability data, the additional hazardous elements that were incorporated the fly ash matrix appeared stable. Long-term leaching results showed slight increases in trace element concentrations for the baseline and LAC ashes, while the lime ashes showed decreasing trace element concentrations. This is mainly due to the secondary hydrated phases formed that are a function of the chemical composition and pH level. These observed increases/decreases should not pose any foreseeable long-term potential problems related to disposal.

- Little difference was noted between the chemistry and leaching properties of the baseline ash and the ash with LAC and SO_3. Although mercury concentrations for the LAC cases were significantly higher than for the baseline cases, the concentrations were well below RCRA limits and the mercury appeared to be in a stable form. The addition of LAC did not change the mineralogy of the ash compared to the baseline ash.

- The addition of lime significantly changed the chemical composition and pH level of the fly ash, therefore significantly changing its utilization potential. These fly ashes did not meet ASTM C 618 specification for use as a mineral admixture in concrete. Other utilization options (mineral filler in asphalt, soil stabilizers, structural fill, controlled low-strength material, etc.) should be considered. Disposal methods currently employed should be adequate.

Task 30 – Hot-Gas Filter Characterization Project

This project was designed to perform the research necessary to determine the fuel-, sorbent-, and operations-related conditions that lead to blinding or bridging of hot-gas particle filters. The primary deliverable was a graphics-driven computer model that can be used to predict problems and develop control strategies based on data from the analysis of coal and sorbent as well as system conditions. The research was designed around five tasks. Task 1 consisted of sampling at large-scale hot-gas filter test units, gathering representative archived samples from completed programs, and physically and chemically characterizing the samples. Task 2 involved thermochemical equilibrium modeling of appropriate test procedures along with laboratory measurement of the rates and mechanisms of tensile strength development in ash cakes. Task 3 involved dynamic bench-scale testing of the formation of ash in PFBCs and determining the factors affecting the rates of residual cake development under both FBC and gasification conditions. Task 4 involved creating a graphical interface computer code to tie all of the knowledge together and make possible the prediction of rates of filter blinding and bridging based on coal, sorbent, filter, and system parameters. Task 5 involved reporting the results.

EPRI was the prime project contractor. All research was carried out by the EERC. The EERC, through its DOE JSRP, was able to approximately match funds contributed by the commercial sponsors: EPRI, Lurgi–Lentjes–Babcock (LLB), PowerGen, Schumacher America, Westinghouse, Electricité de France, the Netherlands Energy Research Foundation (ECN), ABB Carbon, and the Electric Power Development Company (EPDC). Because of the addition of three sponsors since the beginning of the project, the EERC requested and was granted at the October 1995 meeting an extension to the project to the end of 1997.

Previous work has shown that the primary forces responsible for ash sticking are electrostatic attraction, van der Waals attraction, liquid bridging, and solid bridging between ash particles. Small changes in fuel or sorbent properties or system operating conditions affect the magnitude of the forces in different fashions. As fuel, sorbent, and operating conditions change, one force may become relatively less important and another force relatively more important. In addition, the magnitudes of many of the forces are dependent on each other. Because of the complicated interplay of these forces, simple rule-of-thumb predictions of possible ash-sticking problems are often inadequate, especially when fuels or sorbents are switched. A search of the literature shows that much of the previous work was geared to relate one bulk property of a filter cake, such as average particle size or porosity, to another property of the cake such as tensile strength. Since most problems are caused by only certain size or composition ranges of ash and the previous work did not address the size and composition distributions of the ash, the previous work was not able to relate these ash characteristics to the original fuel and sorbent, which would have allowed pretest predictions to be made about the likelihood of filter bridging.

The Hot-Gas Filter Ash Characterization project was designed to add to the previous work in areas that are unique strengths of the EERC. These strengths are measuring both size and chemical composition distributions of individual ash particles in cakes and sinters, determining the types of chemical reactions that occur within an ash cake, performing parametric testing with extensive laboratory- and bench-scale simulation facilities and, most importantly, a great deal of experience in relating the properties and reactions of the ash back to the properties of the coal, sorbent, and operating conditions of the system.

To make this information most useful to filter system engineers, it was decided to integrate the knowledge gained about the mechanisms of ash formation and sticking into a computer program that uses input data about the coal, sorbent, and system operation to calculate a simple index of the likelihood of ash-sticking problems in hot-gas filter systems. We believe that by relating the properties and reactions in the ash cake back to the starting feed materials and conditions, methods of predicting possible sticking problems can be developed that will be used in an a priori fashion to help in the selection of coals, sorbents, and operating conditions to maximize system efficiency and availability. The predictions will not replace large-scale testing of filter systems, but can be used initially to narrow the scope of the tests that have to be performed to fine-tune system operation. As experience is gained, the predictive capability can be used to more closely specify fuels or operating conditions to prevent sticky ash problems.

Ash Formation in PFBC Systems

In order to determine how certain fuel, sorbent, and system conditions affect the final size and composition distributions of ash particles leaving a PFBC, computer modeling of ash vaporization/condensation behavior was performed, and tests were done with a bench-scale pressurized fluidized-bed reactor (PFBR) to measure relative fragmentation and coalescence of inorganics and to test alkali getters.

Thermochemical equilibrium modeling was performed to determine whether it is possible for liquids to form on the surface of ash particles under hot-gas filter conditions. The Facility for the Analysis of Chemical Thermodynamics (FACT) computer code was used to predict phases which may form on ash particles with the lowest melting temperature in an SO_2–CO_2–O_2–H_2O atmosphere. Calculations were based on the composition of the coal fired at the American Electric Power Tidd plant. Sorbent material was not included in the system modeled because under equilibrium it would absorb all of the sulfur dioxide, whereas in a real system, the absorption is not 100% efficient and some always exists in the gas phase.

The calculations show that as much as 6% of the ash material can be liquid salts at equilibrium under hot-gas filtration conditions. For the Tidd system, potassium and sodium sulfates are expected to dominate the liquid. Experimental verification for the formation of a K_2SO_4–Na_2SO_4–K_2CO_3–Na_2CO_3 liquid phase has shown that a sulfate–carbonate blend with a composition similar to that of the liquid salt predicted at 727°C is only stable in the presence of SO_2–CO_2–O_2 (5000 ppm/ 20 vol%/balance) atmosphere for about 10 minutes at atmospheric pressure. After the blend is cooled to room temperature, x-ray diffraction analysis shows that portions of the salts form some crystalline intermediate phases: $NaK(SO_4)_x(CO_3)_y$ and $NaKCO_3$. For short reaction times, the composition seems to correspond to the reaction equilibrium determined by FACT calculations. For longer reaction times, the intermediate phases disappear, and a final product rich in sulfates is formed that will tend to have a higher melting point, possibly causing the melt to freeze as the loss of carbonate occurs.

Ash formation testing. Information about the transformations occurring in the coal inorganics in the bed and in the filter system in a PFBC had to be determined on the bench scale. The research was performed at the EERC with a PFBR employing a bench-scale hot-gas filter vessel (BHGFV). The PFBR simulates the bed chemistry, ash interactions, and emissions from a PFB under closely controlled conditions. Fourteen ash formation tests were performed to measure the relative contributions of coal and sorbent properties and bed temperature to the size and composition distributions of the ash leaving a PFBC. This information was used to quantify the various ash transformation mechanisms so that algorithms could be developed to predict the final size and composition distribution of ash entering a filter vessel based on coal and sorbent analyses and system conditions.

Pittsburgh No. 8 coal from the CONSOL Enlow Fork mine was obtained for the ash formation testing. A sorbent calcium-to-sulfur ratio (Ca/S) of 2 was used by premixing either of two different-sized Plum Run dolomites with the Enlow Fork mine coal. This coal and sorbent were very similar to those used at the Tidd plant. In addition, Belle Ayr, Wyoming, subbituminous coal was obtained from the Wyodak seam to determine coal-type effects. In addition to the coals, specific lithotypes or bands of coal were collected from the Enlow Fork mine and from the Wyodak seam of the Eagle Butte mine, Wyoming, to determine the effects of maceral composition on ash formation. They include two vitrinite-rich (superbright and bright) lithotypes and a durain (dull) lithotype.

There was no significant difference in particle-size distribution measured for the entrained particulate leaving the combustor because of operating temperature or sorbent size for the Pittsburgh No. 8 coal. There is a significant difference in particle-size distributions between the two coal types, with the Belle Ayr coal producing more of the largest and finest size while the Pittsburgh No. 8 produced more of the intermediate-sized ash. There also is a significant difference in the ash formed from lithotypes from the different coals but not between different lithotypes from the same coal.

The samples were chemically analyzed by SEM, which gives quantitative information about the bulk composition as well as the composition distribution of the ash particles. For the Pittsburgh No. 8 tests, the data show that most of the dolomite ends up in the largest size fractions of ash leaving the combustor, while more of the aluminosilicate ash derived from the coal minerals are in the smaller size fractions. There is also some evidence that sulfated aluminosilicates such as nosean and haüyne are also in the finest size fraction. For the subbituminous coal tests, most of the sorbent is also collected in the largest particle-size range, while most of the organically associated calcium in the coal ash is found in the intermediate size ranges. The smallest size range is primarily condensed vapor-phase sodium and potassium sulfate.

Alkali gettering. The PFBR and BHGFV system was also used for another DOE-funded project to determine the efficiency of certain materials in removing alkali from PFBC flue gases to a level specified by turbine manufacturers (24 ppbw). The Hot-Gas Filter Ash Characterization project provided limited analytical support to this project because some of the data showed that the alkali sorbent materials (getters) can also affect ash bridging between filters.

Several aluminosilicate minerals were studied as sorbents because of their potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation. The alkalies are absorbed onto the surface and diffuse into the bulk of the alkali getter. Initially, it was thought that some materials may be able to absorb both alkalies and sulfur and chlorine, but early results indicated that simultaneous removal of alkali and sulfur and/or chlorine was not practical under the conditions for commercial PFBC operations. In-bed alkali getters had the greatest impact on filter performance, especially bridging and blinding.

The overall conclusion from this work is that in-bed alkali getters can effectively reduce vapor-phase alkali concentrations. This reduction is of a magnitude great enough to control ash deposition and agglomeration and filter blinding, but not to a level low enough to meet current turbine manufacturer recommendations for vapor-phase alkali. Bauxite is considered the best getter tested on the basis of its ability to control all of the above-mentioned problems. Kaolinite is less effective because of its tendency to form deposits from its fine fraction. Finally, although sodalite and nosean can be formed and result in combined sodium and chlorine or sulfur capture, they do not form at a rate high enough to make them effective getters under PFBC conditions.

Measurements of Ash Partitioning in PFBC Systems

Because of aerodynamic sizing, the ash collected or deposited at different positions within a PFBC system do not often match the size distribution of the bulk ash produced during combustion. Larger particles tend to remain within the bed, whereas the smaller particles are carried out and into downstream cyclones and filter systems. This process, called partitioning, affects the composition distribution of the particles forming the deposits because of the mineral-specific degrees of vaporization/condensation, fragmentation, and coalescence reactions that occur. In order to accurately predict the size and composition distribution of the ash forming ash bridges, the partitioning of the ash within the system was measured. Since carryover from the combustion bed and capture in cyclones are fairly well understood, we focused on three types of partitioning within filter vessels: variations in ash size and composition with position in the vessel, variations between the bulk ash and that forming the residual cakes, and variations within a cake.

Variations in a filter vessel. The Ohio Power Company and American Electric Power donated a large number of ash and coal samples from several test series of the Tidd PFBC demonstration plant, including full sample sets of a variety of residual cakes and ash deposits that had formed during three test series in the Westinghouse advanced particle filter (APF) assembly.

The APF experienced some ash bridging and pressure drop increase during the test series ending in May 1994, and there was some buildup of ash on all of the filters. In general, all of the deposits had nearly identical compositions, and all were essentially the same as that of the bulk ash entering the filter vessel (as represented by the hopper ash composition). This shows that with the upstream cyclone in position to remove the larger ash particles, little partitioning occurred within the filter vessel because all of the ash entering the filter vessel was small and capable of reaching any position in the filter vessel. In tests performed in early 1995, the system cyclone located upstream of the APF was completely spoiled, allowing a much higher ash flux and much larger particles into the APF. The compositions of the reduced deposits and cakes remaining in the APF in May 1995 were much more varied than when the system cyclone was in place. The greater variation occurred because different sizes of ash were concentrated in different types of deposits and cakes and because of variations in filter permeability (a number of different filter types were included in these tests).

Formation of residual filter cakes. The composition of the ash-forming residual cakes and collar deposits can vary greatly from that of the average ash composition entering the filter vessel. However, the study of archived samples such as those collected from Tidd did not allow us to determine the specific size ranges of ash that formed those deposits, since much agglomeration had occurred after deposition. Therefore, the EERC PFBR was used to produce ash cakes during a 100-hour run while operating with a fuel and sorbent similar to those used at Tidd. During the run, hundreds of grams of entrained particulate entering the filter vessel was collected, sized with a multicyclone, and quenched. This allowed us to make comparisons of the compositions of the different size ranges to those of the residual cakes, as well as to provide quenched ash samples for testing in the laboratory.

The variations in compositions of the different aerodynamic size ranges of the quenched ash are striking, indicating that the smaller size ranges are greatly enriched in coal ash and depleted in sorbent material as compared to the larger size or as compared to the weighted average of the feed material. However, 90% of the particulate collected in the multicyclone sampling system is captured in Cyclone 1, and that size range has a composition similar to that of the fuel and sorbent, so that the overall effect is that only slight partitioning of elements occurs between the combustor and the filter vessel because of size enrichment.

Partitioning between the ash entering the filter vessel and that forming the residual filter cake is also striking. The average composition of the residual filter cake indicates that it is highly enriched in particles with aerodynamic diameters of less than 20 µm even though that fraction of the ash comprises, at most, 10% of the total entering the filter vessel. In addition, the residual cake is much more highly sulfated than the ash entering the filter vessel, demonstrating either that the sulfation takes longer than a typical backpulse cycle or that the smaller ash sulfates more quickly than the larger ash, which makes it stickier so that it tends to remain behind after backpulsing. Malvern analyses of a cake show that the cake particles are highly agglomerated, indicating either that agglomeration occurs in the cake after deposition or that agglomerated particles are stickier. The agglomeration illustrates why it is difficult to discern from filter ash what the sticking mechanisms are or what the source of the residual cake or bridge ash is since the particles have reacted in situ, changing both chemically and physically from how they first arrived into the vessel.

Variations within a filter cake. An intact cake formed during the 100-hour cake formation test with the PFBR was analyzed by SEM. Variations in cake density can clearly be seen as bands parallel to the surface of the filter. The bands represent regions of different density, but with the exception of phosphorus, there was no variation in composition between the bands. Nor could the number of bands be related to any variations in recorded operating conditions. The banding phenomena need to be explored more closely in a follow-on project because it is likely that one type of band is weaker than the other, and if we can determine what causes the formation of the weaker band, we may be able to exploit the phenomena to cause the cakes or bridges to be weak enough to easily shed under their own weight.

Particulate Sticking and Sintering Mechanisms

The factors most affecting sticking and sintering of particulates are van der Waals forces, liquid bonds caused by condensation of alkali salts, and solid bonds caused by solidification of the salts, gas–solid reactions, and silicate sintering. Because of the complexity of the interactions of these forces, a full-factorial test matrix encompassing all of the possible factors affecting the magnitudes of the forces would have been too large for measurement under this project. To reduce the number of variables, the EERC approach was to measure the relative influence of the most important factors on cake tensile strength under conditions as close as possible to those experienced by actual filter cakes and ash bridges.

In situ sulfation reactions. SEM analyses of ashes collected from filters showed that sulfur pervaded the silicate-based coal ash and was not just associated with the sorbent. The degree of sulfation indicates that all of the Ca and Mg were completely sulfated, whether they exist as relatively pure sorbent-derived particles or the Ca and Mg are dissolved in aluminosilicate ash particles. The data show that both sorbent-derived and aluminosilicate ash particles that contain Ca and Mg can be sintered together through the mechanism of in situ sulfation.

In order to determine the critical temperatures of sulfation, as well as the effects of sulfur dioxide and water vapor concentrations on these temperatures and the amount of sulfation, samples of quenched entrained ash particles collected at the entrance to the filter vessel during the 100-hour PFBR test were tested in a pressurized thermogravimetric analyzer (PTGA). The data show that for low sulfur dioxide concentrations, decomposition occurs upon heating in the PTGA, whereas for higher concentrations, additional sulfation occurs. The amount of sulfation is directly related to the sulfur dioxide concentration. This implies that the degree of sintering of the ash in situ would also be directly related to the concentration of sulfur dioxide in the gas stream. The presence of water increases the degree of sulfation of the ash above 600°C probably by increasing the permeability of the sulfated layer. This indicates that higher water vapor concentrations in the gas stream will increase the amount of sintering of the ash caused by in situ sulfation.

Initial sulfation of the ash occurs within 5 minutes of its depositing on the ash cake. This implies that unless backpulsing can be done every few minutes, some sulfation, hence sintering, of the ash will occur in situ. Since such short backpulsing periods would substantially increase operating costs, rapid backpulsing is probably not a good way to prevent all sintering caused by sulfation in the residual cake deposits. However, this is only about one-third of the total sulfation expected, so the final sulfation must occur over periods of hours. It is not clear at this time how much of the sinter strength is contributed by short-term versus long-term sulfation.

Although the sulfation studied with the PTGA results in the formation of a solid material via a gas–solid reaction, the thermochemical equilibrium modeling indicated that some condensation of sulfate salts could also occur, forming thin layers of surface liquid. It is expected that the liquid salt would wet sorbent-derived particles, but it was not initially clear if liquid salt would wet silicate-based ash particles. If the salt does not wet the ash, then it cannot form a liquid bridge. To determine the wettability of aluminosilicate ash by molten salts, a pellet of pure sodium sulfate was melted on a button of fused slag made from Illinois No. 6 coal ash. Immediately after melting, the molten sulfate did not wet the silicate, but over approximately 10 minutes, it reacted with the silicate material to form an intermediate compound (this is confirmed by SEM analyses), and the surface then became wet. This relatively short reaction time indicates that filter backpulsing periods would have to be relatively short to prevent liquid salt bridges from forming between silicate particles.

Factors affecting the tensile strength of ash cakes. The primary variables tested were cake temperature, cake porosity, particle-size distribution, in situ chemical reaction, presence of surface liquids, and water vapor effects. To measure these relative effects on cake tensile strength, two types of apparatus were designed and constructed under this project: the high-temperature tensile tester (HTTT) to measure short-term effects and long-term pellet sintering equipment.

In related EERC research on baghouse efficiency, it was identified that an ash cake tensile strength between 0.5 and 1.0 g/cm^2 is recommended to ensure the cake does not disintegrate during backpulsing and reattach to the filters. This lower strength range is not expected to change greatly at pressurized hot-gas temperatures because the effects of higher pressure on the density of the gas that would reentrain the ash is largely canceled by the reduction in density caused by the higher temperature. In testing ash collected from the Westinghouse filter vessel at the Tidd plant, it was determined that at strength levels of 2.5 to 3.0 g/cm^2, the ash begins to sinter slightly, and the cake begins to slide along the porous frit bottom of the split-cylinder chamber. This means that the capabilities of the HTTT are being exceeded at this level of strength for this particular source of filter ash. It also indicates that this is the strength necessary to form a bridge for this ash. In later tests with other ashes, higher strengths could be measured with some cakes, different cakes had different plasticities, and tensile strength did not always correlate directly with bridging propensity.

Since many bridges must support themselves against gravity, tensile strength alone does not indicate the likelihood of a cake to form a bridge. What is more important is the strength in relationship to the density of the cake. This quantity, referred to as the cake critical thickness index (CTI), is defined in the equation below:

$$Critical\ Thickness\ Index = \frac{\dfrac{Tensile\ Force}{Cake\ Cross\text{-}Sectional\ Area}}{\dfrac{Cake\ Weight}{Cake\ Volume}}$$

The CTI has units of length and indicates the relative thickness of a cake that can form before shedding under its own weight. A high CTI indicates that the cake is relatively sticky for its weight and is more likely to form a bridge than a cake with a low CTI. Because other forces, especially those related to vibration, act on filter cakes and bridges, the CTI should not be used to predict the actual cake thickness that may occur on an in situ pressure vessel filter. Rather, it is a relative number used for comparing the relative likelihood of filter bridging.

Tidd filter hopper ash collected in February 1995 was evaluated for CTI as functions of porosity and temperature. In general, this ash was not considered sticky and did not form ash bridges. The data show that as the temperature and level of compaction of the Tidd ash increase, the resulting tensile strength also increases. The effect of compaction is much more pronounced at higher temperatures, but generally causes a doubling in the CTI for every 6% decrease in void fraction (porosity) for temperatures above ambient. This increase in CTI indicates that strength increases relative to bulk density as void fraction decreases at higher temperatures, but not at room temperature. However, for a given void fraction, the temperature has a much greater effect, increasing the CTI by an order of magnitude as temperature is increased from ambient to 700°C at a void fraction of 62%.

The tensile strength and density of the cake made from different size ranges of quenched ash were determined with the HTTT at 800°C in a combustion atmosphere. The smaller ash that is known to form residual cakes has up to a 50% greater CTI than that of the bulk ash entering the filter vessel. In addition, the quenched bulk ash has nearly twice the critical thickness of the hopper ash that had chemically reacted on the filters and then been pulsed off and collected in the filter hopper. Also, the smaller, quenched ashes that formed the residual cake had 2 to 3 times the CTI of the filter hopper ash. These results strongly indicate the need to perform strength tests with quenched and sized ash so that factors affecting ash bridging can be more clearly delineated.

In order to determine the effects of surface liquid on the cake's CTI, tensile strength measurements were performed at room temperature on filter hopper ash by wetting it with ethylene glycol and glycerin. The ash was collected during the 100-hour PFBR run discussed earlier. The liquids were chosen for their low vapor pressures and because they have viscosities bracketing the lowest (ethylene glycol at 0.2 poise) and highest (glycerin at 10 poise) viscosities expected for the molten salts. With the addition of 1% ethylene glycol to the filter ash, the CTI increased by approximately 75% on average. This increase could easily turn a nonbridging ash into a bridging ash. However, the ability of the liquid to wet the ash is much more important than the viscosity of the liquid in increasing the strength of an ash cake. Since liquid salts do not immediately wet the silicate ash, but do so over periods of approximately 10 minutes (we expect that the sorbent-derived particles would be immediately wetted), the strength of the ash cake would increase because of wetting over this same time frame.

The Filter-Bridging Index Code

In order to make the data developed in the project most useful to actual system engineers, it has been reduced to a series of algorithms, which are assembled into a computer code. The Filter Bridging Index Code (FBIC) uses several different modules to calculate the relative probability that a filter ash will be sticky enough to bridge across candle filters as a function of the temperature of the ash. It uses input data from the analyses of the coal and sorbent and some system conditions. First, the input data are used to calculate the particle-size and composition distributions of the coal ash entering the filter vessel of a PFBC based on the data from the bench-scale activities. Then, several program modules are applied to the data to calculate the relative stickiness of the ash caused by physical attraction (van der Waals and electrostatic forces), liquid bridging by alkali metal and alkaline-earth sulfates, and solid-state sintering by lower-viscosity silicates. The relative stickiness calculated is based on the laboratory work. A copy of the program was included on a diskette accompanying the final report.

Task 31 – Formal Evaluation of Flue Gas Chemical Measurement Methods, Phase 1 – Verification of Mercury Speciation by EPA (Draft) Method 29

Reliable methods for determining mercury emissions from fossil fuel-fired electric utility power plants are required to achieve a 1990 CAAA goal of assessing potential human health risks from exposure to mercury. The U.S. Environmental Protection Agency has developed and validated two methods, EPA Method 101A and EPA Method 29, for determining total mercury emissions. In addition to accurately measuring total mercury, the quantification of individual physicochemical forms (i.e., species) of mercury is crucial for addressing fundamental questions relating to mercury bioaccumulation, emission control, and atmospheric fate and transport, because each form has distinctive physical, chemical, and biological properties. Accurate measurements of the mercury species present in fossil fuel-fired power plant emissions are scarce because of a lack of reliable sampling and analysis methods for the different mercury species.

To facilitate method development, a research program funded by EPRI and DOE was initiated at the EERC to evaluate mercury speciation methods that may be applicable for electric utility power plants. The objectives of the project were:

- To determine whether EPA Method 29 or other sampling methods can reliably quantify and speciate mercury in the flue gas from coal-fired boilers.

- To determine the precision and bias of these methods as a function of process variables.

The EERC conducted pilot- and bench-scale tests to first evaluate EPA Method 29 and later four other mercury speciation methods. In addition, for some of the pilot-scale tests up to four different continuous emission monitors (CEMs) for mercury were used to supplement the data from batch sampling methods. The mercury speciation methods tested were EPA Method 29, the Mercury Speciation Adsorption (MESA) method, the Ontario Hydro method, the tris-buffer method, and EPA Draft Method 101B (as described by Research Triangle Institute).

The CEMs tested were the Perkin Elmer MERCEM, the PS Analytical Sir Galahad, the Semtech Hg 2000, and ADA Technologies.

The first series of pilot-scale tests were to evaluate the speciation ability of EPA Method 29 following the procedures outlined in EPA Method 301 (six replicates of quadtrains per test condition). Because it was necessary to do dynamic spiking of Hg^0 or $HgCl_2$ to obtain an indication of the accuracy of the method, mercury-spiking systems were developed that could reliably inject known quantities of either Hg^0 or $HgCl_2$ into the flue gas upstream of the sampling point.

The pilot-scale tests were conducted using the EERC PTC. This unit, which can operate firing natural gas or pulverized coal, generates approximately 5.7 m^3/min (200 acfm) of flue gas at 177°C (350°F). The pulse-jet fabric filter initially used woven fiberglass bags, but later the bags were changed to all-PTFE (polytetrafluoroethylene) GORE-TEX® membrane bags. These bags gave a very high collection efficiency and did not interact with the mercury in any way.

After researchers had determined that the ability of EPA Method 29 to speciate mercury was questionable, they decided to conduct full and fractional factorial bench-scale tests using simulated flue gas. Bench-scale tests set up as either full or factorial designs were conducted using EPA Method 29, the Ontario Hydro method, the tris-buffer method, and the MESA method. The simulated flue gas consisted of 4% oxygen (O_2), 15% carbon dioxide (CO_2), and 10% water vapor (H_2O). The variables tested were as follows:

- Sulfur dioxide (SO_2) – 1500 ppm
- Hydrogen chloride (HCl) – 50 ppm
- Chlorine (Cl_2) – 10 ppm
- Blacksville fly ash – present or not
- Nitrogen oxides (NO/NO_x) – 600 ppm
- Mercury species (Hg^0 or $HgCl_2$) – 20 µg/Nm^3

EPA Method 301 Validation Results for EPA Method 29

As part of the initial attempt to validate EPA Method 29 as a speciation method, six pilot-scale tests were completed, all firing Blacksville bituminous coal. Baseline tests and tests with spiking of Hg^0 into the flue gas upstream of the sampling point were completed, as well as two tests to compare EPA Method 101A to EPA Method 29 for total mercury. The results clearly showed that the precision and bias of the measurements were well within the EPA Method 301 statistical criteria. This was true for the mercury measurements for the individual solutions as well as for total mercury. However, it was also clear that when Hg^0 was spiked into the flue gas, it was not being completely measured as Hg^0. A high percentage of the Hg^0 was being collected in the nitric acid–hydrogen peroxide (HNO_3–H_2O_2) solution. The question was whether this apparent conversion of Hg^0 to Hg^{2+} was occurring in the gas stream or if EPA Method 29 was giving incorrect mercury speciation measurements. At this point, the EPA Method 301 validation tests for EPA Method 29 were ended and bench- and pilot-scale tests were then completed to try to answer that question.

Bench-Scale Results

The bench-scale tests were designed to evaluate what flue gas components affected the ability of EPA Method 29 and the MESA method to speciate mercury or, in later tests, the Ontario Hydro and tris-buffer methods.

Bench-scale tests showed that for EPA Method 29, the addition of 1500 ppm of SO_2 to the simulated flue gas resulted in about 10%–15% of the injected Hg^0 being captured in the HNO_3–H_2O_2 solution and reported as oxidized mercury (Hg^{2+}). This was not observed with the other sampling methods. However, the speciation ability of the MESA method was substantially affected when SO_2 and NO_x were both present.

The effect of fly ash on mercury speciation was apparent for all the methods tested. The bench-scale results showed about 10%–15% measured oxidation of Hg^0 to Hg^{2+}. This effect was proven to be actual conversion across the filter holding the fly ash and not simple adsorption of mercury onto the surface of the fly ash or erroneous mercury speciation results from the methods. The effects of chlorine as Cl_2 on mercury speciation are more complex. There appears to be a substantial effect for EPA Method 29 and the Ontario Hydro method. Although not tested at the EERC, it has been reported that Cl_2 has about the same effect on the EPA Draft Method 101B method. For the tris-buffer method, less of an effect was evident, and none was evident for the MESA method. For the Ontario Hydro method, there appears to be an interaction between Cl_2 and SO_2. The fact that Cl_2 may affect the ability of the Ontario Hydro or other wet-chemistry methods to speciate mercury may not be a concern for coal-fired systems. It is highly inconclusive whether Cl_2 is present in any appreciable quantities at the temperature at which mercury is typically measured in a particulate control device on coal-fired utilities.

On the basis of the bench-scale results, researchers decided that the Ontario Hydro and tris-buffer methods had the most potential to accurately speciate mercury in coal-fired combustors. Therefore, most of the pilot-scale tests that were conducted following the bench-scale tests were to evaluate these two methods.

Initial Exploratory Pilot-Scale Tests to Evaluate Alternative Mercury Speciation Sampling Methods

The exploratory pilot-scale tests were designed to evaluate different mercury speciation sampling methods and to determine what flue gas components interfered with these methods. Bench-scale studies were conducted in conjunction with the pilot-scale tests, and the results from the bench-scale tests were used to help determine what pilot-scale tests were to be conducted.

Most of these exploratory pilot-scale tests were conducted firing natural gas with the purpose of determining the cause of the apparent oxidation of Hg^0 to Hg^{2+} observed in the previous pilot-scale tests. Four different mercury speciation measurement methods were tested. These were the EPA Method 29, Ontario Hydro, and MESA methods. For the first test, only Hg^0 was injected into the flue gas. For the following tests, in addition to the Hg^0 other components added were SO_2, HCl, and fly ash from the Blacksville coal tests. Results indicated that with only Hg^0 injected into the flue, none of the methods showed any appreciable conversion of Hg^0 to Hg^{2+}. When 1500 ppm of SO_2 and 50 ppm of HCl were injected into the flue gas along with 10 $\mu g/Nm^3$ of Hg^0, only the MESA method showed appreciable conversion of Hg^0 to Hg^{2+}. These data agree with those from the bench-scale tests, which showed that the MESA method overestimated Hg^{2+} in the presence of SO_2 and NO_x. The flue gas from firing natural gas generated approximately 250 ppm NO_x. Also, approximately the same conversion was measured at the pilot-scale level compared to the bench-scale level when fly ash was added to the system. On the basis of the bench-scale data and data that were being generated from the pilot plant, it was decided that the use of the MESA method to speciate mercury would not be continued.

Pilot-Scale Tests to Evaluate the Ontario Hydro and Tris-Buffer Methods and EPA Draft Method 101B

Four different coals were used, each presenting different challenges to the mercury speciation measurement methods in terms of the levels of mercury, chloride, and sulfur in the coals and the Hg^0-to-Hg^{2+} ratio generated in the flue gas. The coals tested were Blacksville bituminous, Absaloka subbituminous, Belle Ayr subbituminous coal, and blended Ohio No. 5 and No. 6 bituminous coals.

On the basis of initial exploratory pilot-scale tests and the bench-scale results, it was determined that the Ontario Hydro and tris-buffer methods had the most potential to correctly speciate mercury from coal-fired systems. Also it was learned that EPA had tested a method called EPA Draft Method 101B (the 1N potassium chloride [KCl] impingers used in the Ontario Hydro method are replaced by distilled water impingers) at a cement kiln with fairly good results. Therefore this method was also incorporated into some of the pilot-scale tests.

When tests were conducted with the Blacksville coal using the Ontario Hydro and tris-buffer methods, the data showed that when Hg^0 is spiked into the gas stream prior to the fabric filter, substantial oxidation of the Hg^0 spike occurs. Although not conclusive, this presents strong evidence that the oxidation of Hg^0 to Hg^{2+} occurs in the gas stream (most likely catalyzed by fly ash) and not in the sampling trains. When Hg^0 was spiked at the baghouse outlet, the sampling results were very different. The Ontario Hydro or tris-buffer methods did not measure any significant oxidation of the Hg^0 spike at the outlet of the fabric filter. Both methods under identical conditions (except spiking and sampling location) had shown substantial conversion when spiking was done at the fabric filter inlet, showing that some fly ashes affect mercury speciation.

Once it was discovered that both the tris-buffer and Ontario Hydro methods appear to speciate correctly at the fabric filter outlet, EPA Method 29 was then compared under the same conditions to the tris-buffer method. EPA Method 29 measured approximately 35% of the spiked Hg^0 as Hg^{2+}. The tris-buffer method again measured the entire spike as Hg^0, providing more evidence that EPA Method 29 does not correctly speciate mercury when Blacksville coal is being burned.

The test results for the Absaloka and Belle Ayr subbituminous coals show that the oxidation of Hg^0 to Hg^{2+} was not nearly as significant as it was for the tests firing Blacksville coal. This was to be expected, because the baseline speciation data for these coals indicated that the Hg^0 concentration in the flue gas was much higher than for the Blacksville bituminous coal. Comparing the results obtained when Hg^0 was spiked and sampled at the baghouse outlet to those obtained at the inlet, the results are essentially the same within the data variability. Tests were also conducted for all three coals (Blacksville, Absaloka, and Belle Ayr) spiking $HgCl_2$ into the flue gas stream. The results, whether sampling at the inlet or outlet of the baghouse, showed that the $HgCl_2$ spike could be reasonably recovered (>80% recovery).

In addition to the Ontario Hydro and tris-buffer methods, EPA Draft Method 101B was used to measure speciated mercury for the tests firing the Belle Ayr coal. EPA Draft Method

101B gave mercury speciation results comparable to the those for the Ontario Hydro and tris-buffer methods. However, this coal was not considered a challenge for the method, because it is a low-sulfur coal. Based on the work at Radian, it was thought that distilled water would not collect the Hg^{2+} efficiently in the presence of high concentrations of SO_2 (>1500 ppm). Therefore, additional tests with the Blacksville coal were conducted to compare EPA Draft Method 101B to the Ontario Hydro and tris-buffer methods. The data indicate that EPA Draft Method 101B gives results comparable to those obtained with the tris-buffer and Ontario Hydro Methods for Hg^0. This is in agreement with previous results. However, it should be noted that these tests were completed before it was realized that it was necessary to add potassium permanganate ($KMnO_{4)}$ solution to the KCl solution impingers of the Ontario Hydro method to "preserve" the Hg^{2+} in solution. Therefore, the measured concentration of both Hg^{2+} and total mercury were low for the Ontario Hydro method.

The final pilot-scale tests were performed firing a blend of Ohio No. 5 and No. 6 bituminous coals. This fuel was chosen because it has a relatively high concentration of mercury, chloride, and sulfur. This coal generates between 20 and 25 $\mu g/Nm^3$ of mercury in the gas stream. There was also about 100 ppm of HCl and 3100 ppm of SO_2 in the flue gas. This coal was expected to provide a real challenge to the mercury speciation measurement methods. The measurement techniques tested when this coal was fired were the tris-buffer, Ontario Hydro, and EPA Draft Method 101B.

When Hg^0 was spiked into the flue gas prior to the fabric filter, as was the case with the Blacksville coal, all three methods showed significant oxidation of the Hg^0 spike. However, again, as was the case for the Blacksville coal when the Hg^0 was spiked at the outlet of the baghouse, there was very little oxidation.

On the basis of the pilot- and bench-scale tests conducted, it can be concluded that the Ontario Hydro, tris-buffer, and EPA Draft Method 101B all have the potential to provide accurate mercury speciation measurements. Although the EPA Draft Method 101B results were comparable to those for the tris-buffer and Ontario Hydro methods, it did appear that the data were somewhat more variable.

Final EPA Method 301 Evaluation Tests

The final series of pilot-scale tests was to evaluate two mercury speciation methods in a more formal manner. The criteria established in EPA Method 301 were chosen for this purpose. It is important to understand what information EPA Method 301 can and cannot provide when trying to validate a sampling method for which there is no reference method. Although enough sampling is completed to statistically determine the internal consistency of the method, EPA Method 301 does **not** determine the accuracy of the method. To get an indication of accuracy, dynamic spiking of the flue gas must be used, not just analyte spiking. Fortunately, it was found in previous pilot-scale tests that at the outlet of the high-efficiency fabric filter, little conversion of spiked Hg^0 or $HgCl_2$ occurred. This made it possible to get at least an indication of the accuracy of the method by spiking into the flue gas at the outlet of the fabric filter known quantities of first Hg^0 and then $HgCl_2$.

The coal chosen for these tests to provide a challenge to the mercury speciation methods was the blended Ohio No. 5 and No. 6. A decision had to be made as to what method(s) would be tested in the more formal manner. Because of both monetary and practical considerations (space constraints), only two methods could be tested. The Ontario Hydro and EPA Draft Method 101B were chosen for the following reasons:

- The tris-buffer method is complicated and tends to be more difficult to use properly.
- Sampling time for the tris-buffer method is limited for medium- or high-sulfur coals (>1000 ppm SO_2 in the flue gas).
- The Ontario Hydro method was chosen because work at the EERC, Ontario Hydro, CONSOL, ATS, and Babcock & Wilcox all show that the method works quite well.
- The EPA Draft Method 101B was chosen because of the apparent success in the EPA-funded study conducted at the Holnam Cement Facility.

Both methods pass the EPA Method 301 validation criteria for all the tests. For all of the tests, the relative standard deviation (RSD) is less than 50%; however, it is apparent that the EPA Draft Method 101B has more variability compared to the Ontario Hydro method and total mercury concentrations were also consistently lower.

In an effort to determine the source of this variability, the impinger containing HNO_3–H_2O_2 (placed just before the H_2SO_4–$KMNO_4$ impingers) for both the Ontario Hydro method and EPA Draft Method 101B was analyzed. The HNO_3–H_2O_2 impinger solution mercury data show that EPA Draft Method 101B does not speciate mercury as well as the Ontario Hydro method. When $HgCl_2$ is spiked into the flue gas, it is apparent that some of the $HgCl_2$ bypasses the distilled water, but not the 1N KCl solution used in the Ontario Hydro method. The KCl solution of the Ontario Hydro method is more efficient than distilled water at capturing $HgCl_2$.

Pilot-Scale Evaluation of Continuous Emission Monitors for Mercury

As stated earlier, mercury CEMs were used in some of the pilot-scale tests to supplement the data from the wet-chemistry methods for mercury speciation measurement. Two series of pilot-scale tests were conducted where mercury CEMs were also evaluated. During the first test series, only the Perkin Elmer and PS Analytical instruments provided data that could be consistently compared to the impinger-based methods. The ADA instrument required an on-site technician and during the whole test period provided little useful data. The Semtech CEM gave very low total mercury values compared to the impinger methods. The conversion cell that came with the Semtech was not efficient enough at converting Hg^{2+} to Hg^0. This conversion cell was modified by the EERC, and the Semtech worked much better during the second series of pilot-scale tests. From the pilot-scale data, it appears that CEMs can provide results that are typically within 15% to 25% of the values obtained by the wet-chemistry methods if they are operating correctly. However, all these instruments required attention by a technician to ensure good operation. Considerably more developmental work is needed before they are ready for field use.

Conclusions

- The Ontario Hydro method is recommended as the best method for mercury speciation measurement for coal-fired boilers.

- All impinger-based methods tested, if there is good quality control, show good agreement for measuring total mercury.

- EPA Method 29 does not speciate mercury correctly in all cases.

- Both the Ontario Hydro method and EPA Draft Method 101B pass the EPA 301 criteria using dynamic spiking of Hg^0 and $HgCl_2$; however, the EPA Draft Method 101B has more data variability. In addition, the distilled water used in Method 101B is not as efficient capturing Hg^{2+} as KCl solution.

- The tris-buffer method has a relatively short sampling time (45 min to 1 hr) when sampling flue gas with SO_2 levels of >1000 ppm.

- Whether using the Ontario Hydro, tris-buffer, or EPA Draft Method 101B, a preservative must be added immediately after sampling to stabilize the Hg^{2+} in solution.

- It appears that some fly ashes can catalyze mercury oxidation, thereby having a substantial effect on mercury speciation.

- The MESA method appears to overestimate Hg^{2+} at SO_2 concentrations of >500 ppm in combustion processes where NO_x is also present.

- Cl_2 has a significant effect on mercury speciation as measured by the impinger-based methods.

- A very high level of quality control and quality assurance is necessary to consistently obtain good mercury data in flue gas studies.

- The Perkin Elmer MERCEM, PS Analytical Sir Galahad, and the Semtech Hg 2000 mercury analyzers gave results for total mercury that were similar to impinger-based methods in limited testing in the EERC pilot-scale combustor. However, substantial attention by a technician was required for all the instruments. Considerably more developmental work is needed before they are ready for field use.

Task 32 – Organic Sulfur Removal from Coal with Super and Subcritical Water

The goal of this project was to produce a fuel from Illinois bituminous coal that meets the 1.2 lb SO_2/MMBtu emission standard put forth by the Clean Air Act Amendments. The primary objective was to develop a continuous processing method for removing organic sulfur along with chlorine and selected HAPs from physically cleaned coal using water at conditions near the critical point. An added benefit would be a decrease in ash, resulting in improved thermal performance. The physical cleaning method selected for the Illinois Clean Coal Institute (ICCI) program was packed-column flotation using a 4-in. packed column.

Years 1 and 2 of the program conducted at the EERC for deep cleaning physically cleaned Illinois bituminous coal showed that flowing water at conditions near the critical point (374°C and 218 atm) was an effective technique for reducing sulfur as well as HAPs. Batch extractions were performed at pressures and temperatures up to, and including, supercritical under constant-flow (dynamic) conditions. Analysis performed on cleaned solids indicated the sulfur levels could be lowered to as low as 0.6%, with a reduction in mercury content as great as 90%.

Using laboratory- and bench-scale systems, the EERC refined the technology to process physically cleaned coal on a continuous basis in the 350° to 450°C temperature range. The EERC enhanced the heat exchangers and high-pressure slurry pump on the pilot-scale hydrothermal treatment unit (the PDU) to maintain high residence times, temperature, and pressure. The additional heat allows researchers to investigate, with continuous flow, conditions that are closer to the critical point of water (374°C), where extraction properties reach an optimum point. The EERC also modified the pilot-scale system to enhance product quality and recoveries by cleaning the organic material present in the process water using a specially designed catalyst modular system. Several commercial catalysts were tested, with special emphasis on potential poisoning, efficiency, selectivity, and catalyst attrition.

Year 3 objectives were to treat 500 lb of physically cleaned Illinois coal samples using the integrated hydrothermal system at conditions near the critical point of water. Since supplies of Illinois Basin coals were limited, an Illinois No. 6 coal already on-site for another project and coal from the Freeman Coal Company's Industry mine were selected as test coals. Flotation experiments were completed at the EERC using conditions previously used by researchers at Southern Illinois University and elsewhere for Illinois coals. Emphasis in the physical cleaning was on recovering coal with pyritic sulfur levels as low as possible. No attempt was made to maximize ash rejection and coal recovery. On obtaining satisfactory column operation, more than 600 lb of physically cleaned coal was prepared for continuous testing on the pilot-scale hydrothermal PDU. Physical cleaning decreased the total sulfur from 3.4 to 2.2 wt%, with the pyritic sulfur decreasing from 1.7 to 0.7 wt% for the Industry coal and 3.4 to 2.7 wt% and 1.3 to 0.6 wt%, respectively, for the Illinois No. 6 coal. Work at the EERC was interrupted by the spring flood of the Red River of the North in Grand Forks, North Dakota, which was of a magnitude never before witnessed in the region. The entire city, including the research facilities at the University of North Dakota EERC, was flooded. The EERC, along with the remainder of the University, was forced to close because of water in the bottom floors of the buildings causing loss of power, water and sewer, and equipment. Technical work at the EERC was not possible between April 17 and May

8, 1997. From May 8, 1997, forward, the premises were cleaned, electricity was restored, repairs were made, and equipment replacements were begun. As equipment was put back into service, project activity gradually increased. Fortunately, the subcritical extraction equipment used in the ICCI project was not seriously damaged and was prepared for testing as operators became available.

Following flood recovery, shakedown testing of the continuous hydrothermal system to determine operating parameters, including solids loading in the slurried feed, was carried out. Process residence times were increased to over 1 hour by using a Bran-Lubbe high-pressure pump system and adding a high-pressure reactor. Additional heat was applied with a superheater downstream from a series of three Dowtherm preheaters. Initial plugging problems caused by settling of the coal were corrected by increasing the solids loading from <10% to >40%. The EERC treated over 200 lb of cleaned coal at near-critical temperature and pressure using the continuous slurry method with unsatisfactory sulfur removal. The equipment was then reconfigured for batch operations. Continuous hydrothermal cleaning initially was hampered by plugging problems. To overcome this problem, it became necessary to increase solids loading from 10% to 30% and, ultimately, increase heat demand, producing a product with little change in the sulfur content of the solids.

Additional testing at extended residence times and with additives had minimal effect on sulfur removal. This indicates that temperature and mode of operation are primary factors in controlling the removal of sulfur from coal by extraction with water. Continuous operation includes excessive close contact between solids and sulfur during the processing, resulting in lack of sulfur removal. The batch process offers less long-term close contact and provides a tar–water stream that can be treated by on-line catalytic desulfurization. Near the end of the contract, the EERC completed limited testing with the tubular reactor configured in batch mode to process the physically cleaned coal with water at higher temperatures and reduced coal–sulfur extraction contact time. Although less than 50 lb was processed with the new system, early results indicated organic sulfur removal to be 33% better than the continuous mode. In addition, the EERC added to the process an on-line catalyst module system that desulfurized the aromatic tars.

Reconfiguration of the PDU to accommodate batch processing resulted in solids from the Industry coal with 1.5% sulfur. With a system designed at the EERC, on-line catalytic desulfurization using cobalt–molybdenum on zeolite reduced the sulfur level in the tar from 2.2 to 1.4 wt%. Recovery of solids and tar resulted in 85% mass recovery. The tar and solids were recombined, and briquettes with a heating value of 14,475 Btu/lb were made.

A second objective in Year 3 was to develop on-line catalytic desulfurization capability. Catalysts were tested on the bench scale, while a catalyst vessel for the PDU was designed and built. In bench-scale testing, cobalt–molybdenum catalyst reduced the sulfur content of tar from 1.60 to 0.11 wt% in an aqueous environment, whereas the tar sulfur was reduced from 2.4 to 1.4 wt% by the catalyst in the pilot-scale testing. The desulfurized tars were added back to the solids to increase fuel recovery by 7 wt% (26% increase in volatile matter) to give a total fuel recovery of 85% with only 3.5 wt% ash on a moisture-free basis. Approximately one-third of the volatile matter was water-soluble or converted to gas and, therefore, in these tests was not recovered in the condensed-phase fuel.

A third objective in Year 3 was to remove selected HAPs by the hydrothermal process. Mercury content was reduced from 0.319 µg/g in the raw coal to 0.166 µg/g in the deep-cleaned coal, while chlorine was reduced from 950 to < 50 µg/g. Previous tests with IBC-101 and IBC-102 have shown Hg reduction of 58% and 99%, respectively, indicating that Hg removal is effective by hydrothermal treatment and is dependent on the disposition of the Hg. Chlorine was reduced from 950 µg/g in the feed, to 710 µg/g in the physically cleaned coal, and to <50 µg/g in the hydrothermally treated product.

The EERC is confident in asserting that the technology of this project has led to several significant achievements. It was demonstrated that:

- Subcritical water can remove 25%–70% of organic sulfur and all pyritic sulfur remaining after physical cleaning.

- Desulfurization of coal tar can be accomplished on-line without additional energy input.

- Removal of selected HAPs from coal can be accomplished simultaneously with sulfur removal.

- Tar and solids can be desulfurized in a one-step process.

- Subcritical water extraction of mercury from coal is coal-specific, likely depending on the mineral association of the element.

Task 33 – Upgraded North Dakota Lignite – Production of Test Quantities

The objective of this program was to produce and then provide test quantities of two upgraded North Dakota lignites for eventual combustion as low-sulfur blend stocks. A final report to DOE, the North Dakota Industrial Commission, Knife River Coal Mining Company, and North American Coal Company was submitted in November 1994.

Approximately 1 ton of an upgraded North Dakota Beulah mine lignite was produced at the EERC and then shipped to Babcock & Wilcox (B&W) for combustion testing. The upgraded Beulah mine lignite, which met or exceeded several target specifications, had the following analysis: 0.49 wt% sulfur (moisture-free), 8.9 wt% moisture, 5.6 wt% ash, 9850 Btu/lb (as-received), 0.91 lb of $SO_2/10^6$ Btu, and 3.5 wt% sodium (as oxide) in ash.

The processing scenario for the upgraded Beulah mine lignite included crushing and classifying, physical cleaning to remove liberated minerals and pyrite, briquetting to improve density and handling, and thermal drying to improve heating value. A Falkirk mine lignite underwent crushing and classifying, physical cleaning, and hot-water drying for irreversible moisture removal. The treated Falkirk lignite was briquetted to produce a stable, transportable fuel for delivery to B&W.

Task 34 – Coal Quality Expert Fouling and Slagging Algorithm Development

The Coal Quality Expert (CQE) model was developed by Black and Veatch under contract from EPRI and DOE. To enhance this model, the EERC developed five computer submodels, which were designed to account for the heat transfer losses due to ash deposition within both the radiant and convective sections of a coal-fired boiler. Each of the five computer submodels is discussed below. Because of incomplete funding from the industrial partner, this project was terminated early, and in some instances only beta versions of the submodels were delivered to Black and Veatch.

SEMINAL

This submodel predicts CCSEM data for a coal based on ASTM analysis of a coal. In general, the CCSEM data are more detailed than conventional ASTM analyses and thus the conversion requires numerous assumptions. This submodel is essentially a best-fit routine utilizing a database of nearly 100 coals. This algorithm is necessary when the CCSEM data are not directly available for a coal. This submodel was delivered to Black and Veatch as a C++ (OS2 platform) source code.

CQECCSEM

This submodel reduces the volumes of data generated during a CCSEM analysis into a summary file to be used by the CQE model as input to FOULER. A full CCSEM analysis commonly has over 50,000 data points, which are reduced to a matrix of 34 mineral types and 6 mineral sizes by this submodel. This submodel was delivered to Black and Veatch as a FORTRAN (DOS platform) executable file only.

Generation of MMT (Mineral Matter Transformation) Files

This submodel massages the available coal information into a format that can be utilized in the MMT section of CQE. MMT is an executable code that was provided to Black and Veatch by PSI Technologies Inc. The MMT code generates the data necessary for operation of the SLAGGO submodel. Because of the complex nature of coal analyses and the variability of analytical techniques, an algorithm was necessary to provide consistent data to the MMT code. An algorithm was provided to Black and Veatch, which in turn coded it into the CQE model.

FOULER

This submodel accounted for the majority of all work performed within this project. Based on the coal inputs, a model was developed to predict the dynamic heat-exchange properties of deposits forming on steam tubes in the convective section of a coal combustion boiler. This submodel was designed from over 100 different subroutines accounting for ash formation, ash transport, ash deposition, strength formation, and sootblower effectiveness. This submodel was delivered to Black and Veatch as a C++ (OS2 platform) source code.

SLAGGO

This submodel predicts the dynamic heat exchange properties of deposits forming on the waterwalls in the radiant section of a coal combustion boiler. The original static algorithms were developed by PSI technologies and were significantly enhanced into a dynamic predictive method. This submodel was delivered to Black and Veatch as a C++ (OS2 platform) source code.

Task 35 – Evaluation of Field Analytical Techniques for Mercury in Soil

The issue of mercury contamination at natural gas industry metering sites has highlighted the need for analytical techniques that can both generate high-quality screening-level data and be applied in a field setting. The economic benefit of applying these techniques can be significant when the savings resulting from minimizing the mobilization and demobilization of field crews is considered. Further, the fact that time, in and of itself, is an extremely valuable commodity, stresses the need for such techniques.

Given this need, the EERC was contracted by GRI with support from DOE and NOVA Corporation of Alberta to undertake a detailed examination of four field screening techniques for mercury in soil. The four techniques were 1) an anodic stripping voltametry technique developed and tested by General Electric Corporation, 2) a static headspace analysis technique developed and tested by Dr. Ralph Turner of Oak Ridge National Laboratory, 3) the BiMelyze® Mercury Immunoassay (Bio) developed and tested by BioNebraska, Inc., and 4) a transportable x-ray fluorescence instrument/technique developed and tested by Spectrace, Inc. These techniques were tested on a suite of samples consisting of 45 real-world samples collected at gas industry metering sites and three National Institute of Standards and Technology Standard Reference Materials. Each of the samples was presented in blind duplicate to each technique, thereby increasing the sample set to 96 samples. The same suite of samples was presented to each of two fixed laboratory techniques: EPA Method 7471 and a modified version of EPA Method 7471 developed by the EERC that employs larger sample sizes.

The results of the study indicate that each of the tested field techniques is capable of providing reliable screening-level data. Relatively large variation in analytical results observed in collected samples reflects the extreme heterogeneity of mercury occurrence in contaminated soils, particularly when it is primarily in the elemental form, such as at natural gas industry sites. It follows that the sampling strategy at a specific site and homogenization play more critical roles in representative site characterization than does the choice of analytical technique. As such, any technique applied, whether a field screening technique or a fixed laboratory technique, should be applied to numerous replicates of the “same” sample. The choice of a technique for actual application will ultimately be based on a combination of factors, including economics, precision, accuracy, detection limit, and ease of use.

A final report was submitted in June 1997.

Task 36 – Combustion Characterization of Carbonized RDF from Temperature Optimization Tests

The overall objective of this research program was to demonstrate the EnerTech–EERC process of slurry carbonization for producing homogeneous, pumpable fuels from RDF with continuous pilot plant facilities and to characterize flue gas and ash emissions from combustion of the carbonized RDF slurry fuel. Please note that “Wet Thermal Oxidation” is EnerTech’s trademark name for combustion of the carbonized RDF slurry fuel. A final report was submitted in April 1995.

Carbonized RDF slurry fuels were produced with the EERC’s 7.5-tpd (wet basis) pilot plant facility. A hose diaphragm pump pressurized a 7–10-wt% feed RDF slurry with a viscosity of 500 cP to approximately 2500 psig. The pressurized RDF slurry was heated by indirect heat exchangers to between 585° and 626°F and its temperature and pressure maintained in a downflow reactor. The carbonized slurry was flashed, concentrated in a filter press, and ground in an attritor. During operation of the pilot plant, samples of the feed RDF slurry, carbonization gas, condensate, carbonized solids, and filtrate were taken and analyzed.

Pilot-scale slurry carbonization experiments with RDF produced a homogeneous pumpable slurry fuel with a higher heating value (HHV) of 3000–6600 Btu/lb (as-received basis) at a viscosity of 500 cP at 100 Hz decreasing and ambient temperature. Greater-heating-value slurry fuels were produced at higher slurry carbonization temperatures. During slurry carbonization, PVC plastics in the feed RDF also decompose to form hydrochloric acid and salts. Pilot-scale slurry carbonization experiments extracted 82%–94% of the feed RDF chlorine content as chloride salts. Higher carbonization temperatures and higher alkali additions to the feed slurry produced a higher-chlorine extraction.

The carbonized slurry fuel was combusted in a 650,000-Btu/hr atmospheric pulverized coal boiler simulator. From a storage tank, the carbonized RDF slurry was pumped through the burner gun to the atomizer, where it was mixed with atomizing air. Heated primary air carried the atomized slurry out of the burner gun, while heated secondary air was introduced in an annular section surrounding the burner gun. Heated tertiary air was added through two tangential ports located about 12 in. above the burner gun. The combustion flue gases were analyzed on-line for major pollutants, and extractive samples were taken for analysis of trace pollutants. In addition, samples of the combustion ash were taken and analyzed. The objectives and combustion results are summarized below.

- To determine conditions under which a carbonized RDF slurry will be wet thermally oxidized (combusted): During the combustion test of the carbonized RDF slurry fuel, three combustion temperatures were investigated (1600°F, 1800°F, and 2000°F). Excess air averaged 15%–61%, depending on the combustion temperature, and was split approximately 11%, 83%, and 6% among primary atomizing air, secondary swirl air, and tertiary overfire air, respectively. Percentages of excess air were adjusted manually based upon levels of carbon monoxide in the flue gases. As expected, higher combustion temperatures required less excess air to produce excellent combustion performance. In future combustion tests, excess air initially would be set no higher than 35%.

- To characterize flue gas emissions produced from wet thermal oxidation (combustion) of the carbonized RDF slurry fuel: Compared to proposed New Source Performance Standards (NSPS, published September 20, 1994, in *the Federal Register*), carbon monoxide (CO) emissions were 65%–90% lower at 5–17 ppmv at 7% O_2 dry, with carbon burnout exceeding 99.9%. NO_x emissions also were up to 55% lower than the NSPS at 82 ppmv, without selective noncatalytic or catalytic reduction. Since slurry carbonization extracts chlorine from the RDF, HCl emissions were 17 ppmv, or 32% lower than the NSPS, without any acid gas scrubbing. Mercury emissions also were analyzed at 0.003 mg/dscm, or 96% lower than the NSPS. Cadmium, lead, and dioxin/furan emissions were not characterized during these combustion tests. Flue gas emissions from the combustion of the carbonized RDF slurry fuel were well below regulated limits.

- To characterize ash produced from wet thermal oxidation (combustion) of the carbonized RDF slurry fuel: Three leaching tests were performed with a representative sample of the combustion ash: the EPA toxicity characteristic leaching procedure (TCLP), synthetic groundwater leaching procedure (SGLP) for 18 hours, and SGLP for 30 days. Synthetic groundwater was prepared to represent that of Grand Forks, North Dakota, and is unique because of its alkaline pH. For each leaching procedure, no RCRA maximum concentration limit (MCL) was exceeded; thus this combustion ash would be classified as nonhazardous. All SGLP leaching concentrations were lower than those from the TCLP. In general, the ash exhibited very low leaching characteristics and was 89%–99% below the RCRA MCL.

Task 37 – Recent Advances in Research on Ash Deposition in Utility Boilers – Ash Deposition Course

The goals of this EERC project were to develop a short course for transferring technical information from the research community to the industrial community, to seek out the research needs of industry, and to continually upgrade course materials. The Coal Ash Behavior and Deposition short course developed in the project provides an overview of recent research that is increasing the understanding of mineral behavior in coal utilization. This research leads to the advancement of methods to predict ash behavior, which can economically resolve fouling problems for the utility industry.

The goal of the Recent Advances in Research on Ash Deposition in Utility Boilers: Practical Applications for the Electric Power and Coal Industries project is to transfer technical information concerning ash formation and deposition in utility boilers using short course presentations. To improve the communication between researchers and the utility community, EERC personnel have presented 1- or 2-day short courses throughout the United States and internationally. In addition to the presentations, course materials have been continually upgraded with new research information as it becomes available.

The Coal Ash Behavior and Deposition short course provides an overview of recent research that is increasing the understanding of mineral behavior in coal utilization. This research leads to the advancement of methods to predict ash behavior, which can economically resolve fouling problems for the utility industry. Many EERC experts contributing their knowledge to specific sections of the presentation provided input to the course materials. The course materials begin with a description of minerals in coals and then discuss the physical and chemical properties of the materials as they move through the boiler. Emphasis is placed on how these properties affect boiler operation and performance. Discussions are centered on problem-solving techniques and mitigation solutions.

Eleven short courses were held at nine locations throughout the United States during the term of the project. Total course participants numbered 154 and included combustion engineers, boiler operators, fuel specialists, management, other coal researchers, and government personnel. Solicited comments and written evaluations about the content and usefulness of the course by participants were commendatory.

This project has met its goals of developing a short course for transferring technical information from the research community to the industrial community, to seek out the research needs of industry, and to continually upgrade course materials. A final report was submitted in December 1998.

Task 38 – Witnessing, Sampling, and Validating Mercury Remediation Technology Research and Demonstrations

The natural gas industry first became concerned about mercury contamination at gas-metering sites because of the potential for mercury exposure to workers. In addition, under the EPA Land Disposal Restrictions (“Land Ban”), regulations were scheduled to come into force that could severely limit the options for disposal or could require treatment that was either prohibitively expensive or unavailable at any price.

In this context, GRI in late 1991 proposed to fund research identifying the environmental ramifications of existing mercury contamination and investigating options for remediating sites. Several previous research projects at the EERC funded by GRI, DOE, and Union Gas Limited have investigated the range of options available for remediating mercury-contaminated media. In addition, these research projects tested several technologies at bench scale and prototype, including the Mercury Recovery Services (MRS) thermal technology demonstrated at the commercial level. Previous tests showed that both thermal treatment and combinations of physical separation and chemical leaching were effective in reducing mercury in soil to below regulated levels.

The objective of this research was to evaluate the performance of demonstrations of two commercial-scale remediation technologies applied to mercury-contaminated soils from natural gas industry sites. The two companies selected for these demonstrations, MRS and Environmental Technologies International (ETI), both began commercial operations in 1994.

MRS was operating a mobile thermal retort unit at a gas industry client’s remote site in New Mexico. ETI was operating a combination physical separation and chemical leaching technology at a fixed-base facility in Ohio under a RCRA Part B permit, which allowed ETI to accept mercury-contaminated soils and wastes shipped to the facility for treatment. Both MRS and ETI technologies were permitted to operate as recycling processes in several states in addition to New Mexico and Ohio where these demonstrations were conducted.

The MRS thermal retort technology was able to reduce both total and TCLP mercury in soil to very low levels. Total mercury was reduced from about 1000 mg/kg (ppm) to 1–2 ppm. Leachable mercury (TCLP) was reduced from as high as 0.25 mg/L to 0.003 mg/L to nondetect (<0.0001 mg/L), well below the hazardous waste regulated limit of 0.2 mg/L. A Jerome 431-X mercury vapor analyzer was used to spot-check for fugitive mercury vapors during sampling of the demonstration, but readings were low, consistent with 4-day hourly averages provided by MRS, and below the Occupational Safety and Health Administration (OSHA) limit.

The ETI process, a combination physical separation and chemical leaching technology, was not able to reduce total and TCLP mercury in soil to levels as low as the MRS thermal technology. However, ETI projects its rate of throughput to be higher (6–8 tons per hour versus 12 tons per day for MRS). The ETI technology reduced total mercury from as high as 670 ppm in the feed soil to 10 ppm or less in the clay fraction after three leaching cycles. Leachable mercury (TCLP) was reduced from as high as 0.1 mg/L in the feed soil to 0.04 mg/L or less in the clay fraction after three leaching cycles, below the hazardous waste regulated limit of 0.2 mg/L. A Jerome 431-X mercury vapor analyzer was used during the demonstration in two areas where ETI had identified the potential for elevated mercury vapors. Several readings were slightly above the OSHA permissible exposure limit (PEL), but were not considered problematic, since mercury vapor respirators were being worn during sampling within the exclusion zone.

In conclusion, the MRS and ETI technologies differed from each other in many respects (thermal versus physical–chemical, mobile versus fixed, treatment level, long-term liability reduction, secondary wastes, throughput, and cost). However, each company may be able to establish its own niche in the market and be commercially viable, depending upon each client’s sensitivity to the multiple factors listed above. A final report was submitted in March 1997.

Task 39 – Preparation and Gasification of Thailand Coal–Water Fuel

In Thailand, coal is the major source for both power and nonpower usages. Over the past 10 years, the Department of Mineral Resources (DMR) in Thailand has been evaluating the ability of the country's coal reserves to meet its increasing utility and industrial energy needs. DMR discovered over 750 million tons of measured coal and subbituminous reserves. The majority of the reserves are the subject of additional exploration and development plans, which include applying clean coal technologies (i.e., coal preparation and beneficiation techniques) to reduce the impact of coal use on the environment.

DMR and other governmental groups in Thailand are leading the charge to this new coal utilization policy. In September of 1993, officials organized a Clean Coal Technology seminar in Chiangmai and a public workshop in Bangkok. As a result of these meetings, technology needs were identified to enhance coal utilization. One need identified is to produce a coal–water fuel (CWF) from coal for gasification systems. CWFs are the most promising of all alternative coal-based fuels. Converting coal into an easily transported liquid fuel could make it an ideal candidate to replace costly imported oil. The economic merits of CWFs are attractive because, on a heating-unit basis, coal is cheaper than oil. Its quasi-liquid form maintains that differential, since the higher cost of dry bulk coal handling and storage is avoided. The CWF technology opens up new markets to coal producers, while it offers price stability and security of supply for the fuel end users.

The EERC, which has for years been investigating the conversion of coal to energy-dense liquid fuels, was identified as a leading candidate to perform the development program. In response to the inquiry, the EERC prepared a four-task program to assess the responsiveness of the Wiang Haeng coal to the temperature and pressure conditions of hot-water drying (HWD). The treated material was to be slurried in water and gasified at various conditions. The remaining activity focused on Thai personnel training at the EERC in the area of clean coal technologies. The project terms and conditions were accepted in October 1995. Approximately 600 kg of lignite was received in October. Coal was sized and analyzed for testing. A series of six bench-scale HWD tests were completed in October and November. Results indicate an improvement of energy density (slurry basis) from 4450 to 6650 Btu/lb using the EERC-developed HWD technology.

Pilot-scale HWD tests were performed at 300° and 325°C and 7- and 15-min residence times. Results indicated an improvement of energy density (slurry fuel basis) from 4360 to 5830 Btu/lb at 300°C and 6050 Btu/lb at 325°C and a 7-min residence time. The effect of increasing residence time to 15 min was to further increase the heating value to 5980 and 6130 Btu/lb at 300° and 325°C, respectively.

A pilot-scale HWD production run was performed at 325°C with a 7-min residence time. All HWD coal produced at 325°C was formulated into approximately 245 kg (540 lb) of CWF for subsequent gasification testing. The CWF had a solids concentration of 50.8 wt%, an estimated heating value of 6200 Btu/lb, and a viscosity of approximately 510 cP.

Mild gasification tests were conducted using raw and HWD Wiang Haeng coal at 700°C at 30 psig. Two different coal sizes were used in the investigation and two steam:carbon ratios. Gas production was approximately 30% based on maf feed. There was a net loss of water from the process, which indicates that the water–gas shift reaction was occurring. Hydrogen production was very high, accounting for 57%–59% of the total gas production. No clear conclusion can be made on the impact of HWD on the coal prior to gasification because of the differences in gasification conditions.

Based on the success of CWF experiments, the next stages of the development may include testing new coals or testing CWF in a combustion system. Also, additional data are required to evaluate the storage and transportation properties of the CWF. Continued success may lead to extended pilot-scale testing and eventually to commercial demonstration in Thailand.

Specific tasks the EERC and DMR may consider for future gasification program development include the need to define products for specific gasifier types: slurry fuel, solid fuel product (briquettes, fine char), synfuel, or electrical production. Future product testing may include an evaluation of the amount of gas, char, and tar produced at various temperature conditions. Bench-scale tests would then be conducted to optimize tar production versus volatile content of the char. In order to consider synfuel and electrical production opportunities, laboratory tests may include thermogravimetric analysis matrix testing to investigate steam reactivity. Also, a more thorough ash characterization would be needed to assess slagging characteristics.

Personnel from Thailand’s DMR completed interactive training by observing bench- and pilot-scale demonstrations in coal cleaning, briquetting, HWD, CWF preparation and evaluation, and CWF gasification.

Task 40 – Mercury Sorbent Evaluation

This project was conducted by the EERC for EPRI and DOE to investigate the use of sorbents injected upstream of a particulate control device as a means of controlling mercury from coal-fired boilers. The work was funded under two EPRI work orders: the first, titled “Enhanced Air Toxics Control,” was funded under EPRI WO-3453, and the second, titled “Mercury Sorbent Evaluation,” was funded through EPRI WO-8505. The DOE portion of the projects was funded through the DOE–EERC Cooperative Agreement under Task 17, Enhanced Air Toxics Control, and under Task 40, Mercury Sorbent Evaluation. Research under the combined work orders was conducted as a single project. The overall project, initiated in December 1992, was modified several times to include additional work and address changing research needs. Detailed results have been reported in monthly reports, project review meetings, published conference papers, and other interim reports.

Capture of Mercury by Fly Ash

Pilot-scale combustion tests with all three of the coals resulted in some natural capture of mercury by the fly ash. This was demonstrated by both the Method 29 sampling filter and by the baghouse. In all cases for the same coal sample, the capture increased with decreasing temperature. For the two subbituminous coals, the fraction of Hg^0 decreased when there was more fly ash mercury, implying that it was Hg^0 that collected on the fly ash. For both subbituminous coals, significant natural capture occurred even though the fly ash loss on ignition (LOI) was less than 1%, indicating that high-LOI ash is not necessary for natural mercury capture. For the Blacksville coal, the level of Hg^{2+} decreased with increasing fly ash mercury, implying that Hg^{2+} was collected on the fly ash. The Blacksville fly ash had considerably higher LOI (3% to 7%) than the subbituminous ashes. The implication is that the mercury collection mechanisms are different between the subbituminous and bituminous coals. However, the collection mechanisms are not well known.

Pilot-Scale Testing of Sorbents

Initial screening of six different sorbents showed that the lignite-based activated carbon (LAC) and iodine-impregnated carbon (IAC) were the most effective. Further tests with Absaloka subbituminous coal showed that IAC was highly effective, achieving over 90% total mercury removal at 300° and 400°F. However, with the Comanche subbituminous coal, the IAC was completely ineffective, providing no net mercury removal over the baseline case. The IAC appeared to convert all of the Hg^0 to Hg^{2+} for the Comanche coal. For the Blacksville coal, the IAC provided 75% mercury removal at 250°F but only 15% removal at 350°F. For all three coals, the IAC injection resulted in almost no Hg^0 at the baghouse outlet.

The LAC provided over 80% mercury removal at temperatures of 250°F or less for all three coals, but at 300°F, vapor-phase removal was 70%, 50%, and 0% for Comanche, Absaloka, and Blacksville coals, respectively. From these results, we can conclude that the LAC effectiveness is highly dependent on temperature and coal type.

ESP Tests and COHPAC/TOXECON Tests

Very limited testing was conducted with the pilot-scale electrostatic precipitator (ESP) alone. The tests in general indicate that it will be more difficult to achieve high mercury removals with the ESP than with a baghouse. For the COHPAC configuration, the results indicate that mercury removal is somewhat lower than for the same sorbent tested with a pulse-jet baghouse. However, the results are for one coal and sorbent and should not be generalized.

Other Trace Elements

Except for mercury and selenium, the results indicate that trace element removal is in general predicted by baghouse particulate removal. When the particulate removal was greater than 99%, removal of As, Pb, Cr, and Ni was also greater than 99%. Many of the measurements indicated that Cd removal was significantly less than 99%, but the Cd levels were near detection limits. Se removals were in all cases significantly less than the overall particulate removal, ranging from 61% to 97%, indicating that a fraction of the Se remains in vapor form at the exit of the baghouse.

Bench-Scale Injection Tests

Results from these tests were in general quite variable and not a source of definitive information. Several effects made interpretation of the results difficult. The sorbent was premixed with fly ash to facilitate feeding a very small amount of sorbent, but the fly ash itself was found to either collect additional mercury or convert Hg^0 to Hg^{2+}. Therefore fly ash effects could not be readily distinguished from sorbent effects. Some of the injected ash and sorbent mixture collected on the walls of the filter holder rather than on the filter alone. This made it difficult to determine exactly how much sorbent was exposed directly to the simulated flue gas. The Ryton® fabric itself was capable of reducing the $HgCl_2$ to Hg^0, making it impossible to test Hg^{2+}. No conversion was observed with the GORE-TEX® fabric, but the injection problems and fly ash effects remained. Therefore, this experimental approach is not recommended for further testing.

Results from the fixed-bed tests provided repeatable data on the capacity of IAC and LAC for both Hg^0 and $HgCl_2$ for several temperatures and sorbent concentrations. One of the important observations from the LAC tests is the initial sorption of Hg^0 followed by conversion and desorption. This indicates that the interaction of the sorbent, mercury, and other gas components is complex. While the fixed-bed tests can provide repeatable results and indicate relative capacity, temperature effects, and flue gas effects, the mechanisms are not well known.

Bench-Scale Residence Time Tests

Only very preliminary tests were conducted with this system, but initial results indicate it is not a useful approach to determine residence time effects.

Task 41 – Lignite Resource Characterization Evaluation for Mitigation of Ash Disposition

Montana–Dakota Utilities Co. (MDU) had been experiencing severe ash slagging and fouling in its cyclone boiler at the Coyote Station while burning lignite coal from three seams in the Knife River Coal Mining Company (KRCMC) Beulah mine. The EERC evaluated MDU plant and KRCMC mine operations. A dual approach of assessing coal quality and examining plant operating characteristics was implemented to formulate mine-planning, coal-blending, and boiler-operating strategies to mitigate the slagging and fouling.

A historical review of Beulah mine and Coyote Station operations revealed several areas in the mine that may have contributed to slagging- and fouling-related deratings and outages. Samples of coal from these potential “problem areas” and other areas were analyzed in detail to assess coal quality. A boiler inspection program was initiated at the Coyote Station to provide up-to-date, objective information on ash deposition severity and boiler operating conditions. Field tests were completed and operating data obtained during periods of good operation and troublesome operation and differences in operating parameters and coal quality assessed.

Samples of the three lignite coal seams exposed in each of seven drill holes from the Orange and Charlie areas of the Beulah mine were analyzed using standard ASTM methods (proximate, ultimate, and ash elemental oxide composition), CCSEM, and chemical fractionation. In addition, a single in-pit sample from the Red pit area was similarly analyzed, and the ash elemental oxide chemistry determined for a parting layer in Seam 1 of the Orange pit area. The uppermost Seam 1 coal (Schoolhouse Bed) is generally enriched in ash, sulfur, silica, and alumina but depleted in nitrogen, oxygen, calcium, and sodium relative to the underlying Seam 2 and Seam 3 coals (Upper and Lower seams, respectively, of the Beulah–Zap Bed). The CCSEM and chemical fractionation analysis results indicate that a larger proportion of the Seam 1 coal ash in a given drill core is derived from discrete supermicron minerals relative to Seams 2 and 3. The enrichment of submicron minerals and organically bound inorganics in Seams 2 and 3 is conducive to a greater fouling propensity. Analysis of the sample from the coal seam parting indicated a composition of aluminosilicate clay.

Theoretical modeling of slag viscosity predicts that the slag produced from the Seam 1 coal ash in a given drill core is more viscous than the slags produced from the corresponding Seam 2 and 3 coal ashes at a given temperature. The modeling results also suggest that the furnace exit gas temperature (FEGT) of the Coyote Station boiler can profoundly affect slagging and fouling severity. Advanced indices recently developed at the EERC predict that the severity of slagging and fouling at the Coyote Station is less for the Seam 1 coal in a given drill core relative to the corresponding Seam 2 and 3 coals.

Boiler data were collected at Coyote to assess the effects of coal quality and boiler operation on ash deposition. Results point to several operational parameters that need to be closely monitored over extended periods of time to note boiler efficiency impacts. These include excess air, FEGT, the distribution of recirculated flue gas between tempering and recirculation ducts, and the possible maldistribution of recirculated flue gas within both the recirculation and tempering plenums. Review of FEGT measurements, both calculated and measured, indicated extended periods during which temperatures exceed 2100°F. Careful measurement of oxygen in the boiler during field testing showed concentrations approximately 1.0% to 1.5% higher than what plant measurement devices were showing. EERC measurements were obtained using a portable gas analyzer with results reported on a dry basis. These differences may be explained if the Coyote Station analyzers report on a wet basis.

Under a separate small contract with MDU, a coal-sampling apparatus was designed and built. This was used at Coyote to sample from four different coal feeders. The device performed well, except that an alternate dust collection system will be needed to eliminate early pluggage and dust release. Testing has shown that consistent coal sampling and boiler inspection logging is vital at Coyote for determining operation and coal quality impacts. The use of oil in the cyclones to improve burner performance may be related to ash deposition, although no clear trend was supported by the data reviewed at the EERC.

Furnace gas temperature measurements and ash deposits collected in the superheater and reheater regions of the boiler coupled with ash viscosity modeling showed that critical temperature ranges occur in the boiler for certain ash chemistries, above which ash deposition can accelerate to severe proportions. Aluminosilicate and silicate material rich in calcium and magnesium as well as sodium develops fairly low-viscosity liquid phases in the 2000°–2300°F range at or near the furnace exit and slightly beyond. These low-viscosity liquid phases trigger rapid deposit development events, which could possibly be avoided with heavier sootblowing and gas tempering during periods when the critical temperatures would be exceeded.

Fly ash samples were collected in front of the air heater, just below the oxygen-measuring probes. Samples averaged about 2.34% carbon in ash (loss on ignition) and had some unusually large spherical grains, which may be responsible for wear on the gas recirculation fans.

Algorithms for predicting the slagging and fouling propensities of lignite coal in the Beulah mine have been developed. Although the EERC slag viscosity model and advanced indices may be useful for assessing coal quality, it is not economically feasible to apply them to the large number of samples required to adequately characterize the quality of the Beulah mine reserve coal resources. Correlations of the predicted slag viscosities and advanced slagging and fouling index values to standard ASTM analysis parameters have been established to develop cost-effective indicators of lignite coal quality. The validity of the parameters identified as indicators of slagging and fouling propensity was assessed by actual testing at the Coyote Station.

A coal quality and blending program has been completed for KRCMC to assess coal quality based on standard ASTM analysis parameters and to determine optimum blending proportions for the accessible coal seams in the Beulah mine. An analogous version of the program was also developed for MDU to assess blended coal quality based on daily analyses at the Coyote Station.

Task 42 – Holocene Cyclicity in Western North Dakota – Climate Change Interpreted from Fluctuations in Alluvial Sedimentation

This project undertook a close examination of the relationship between Holocene alluvial sedimentation and climatic variation. Although various techniques have been employed to interpret climate during postglacial times, the few studies in semiarid badlands terrains have focused on a general understanding of the broadscale climatic history. This project interpreted finer sedimentary patterns to recognize and interpret climatic variations that may occur as short-period cycles. Such interpretations provide a new approach to examining climatic variability in the past, reflecting periods of extended dry and moist conditions, and will result in the development of a more rigorous basis for interpreting human interactions with both their physical and biotic surroundings.

Basic Climate/Paleosol Premise

Key or basic underlying premises to this study are discussed in the main body of the report. During periods when landforms (landscapes) are stable, hillslopes are covered by a protective mat of vegetation and a balance is established between weathering (soil formation) and valley sedimentation. The weathering of surface sediments during periods of landscape stability produces soils. During periods of landscape instability, vegetation is significantly reduced, if not removed completely, particularly in semiarid regions such as western North Dakota. This leads to slope disequilibrium as erosion outpaces soil formation. Disequilibrium results in the total and/or partial truncation of soils, which, in turn, accelerates the lateral transfer of sediment to lower slopes and valley bottoms. Times of landform stability, or vegetation cover, are generally considered times of moist and cool environments. Conversely, times of dry and warm conditions promote landform instability.

Short-Term Cyclicity

Late Holocene sediments in the badlands terrain of Theodore Roosevelt National Park, Billings County, North Dakota, and in prairie settings of Knife River Indian Village National Historic Site, Mercer County, North Dakota, and along the north shore of Lake Sakakawea (Missouri River), McLean County, North Dakota, preserve records of numerous paleosols buried by alluvial deposits. Along the headwaters of Knutson Creek in Roosevelt Park, Ab horizons occur in minor sections (<1.4 m) with as many as ten paleosols. Although these were not dated directly, a date from a nearby section suggests formation of the paleosols over the last 1430 years (all dates are from AMS radiocarbon analyses). The Knife River Elbee Bluff Locality contains eight Ab horizons in a 2.4-m section, the middle portion of which has five thin, evenly spaced paleosols from about 2000 to 2974 years before present (YBP). The Lake Sakakawea Douglas Creek Locality consists of a stacked, apparently conformable sequence of 15 Ab horizons in a 2.8-m section that can be traced laterally across a small paleovalley. The occurrence of paleosols at this locality can be interpreted over a span of 2655 years (± analytical error). In the prairie setting of Douglas Creek, landform instability may have resulted in alluvial deposition on average about once every 170 to 180 years. The paleosol record preserved in both badlands and prairie localities indicates that soils seem to have been the result of relatively stable environments interrupted by brief episodes of burial every 140 to 200 years. The regularity of these burial events may stand as possible proxy indicators of minor climatic variation on an otherwise general record of climate stability. Stable carbon studies of these paleosols indicate generally cool and moist conditions ($-22.6 \pm 0.6\ \delta^{13}C_{PDB}$‰), except for those forming about 2585 YBP (Douglas Creek) to at least 2165 YBP (Elbee Bluff), during which warmer and drier conditions ($-20.0 \pm 0.4\ \delta^{13}C_{PDB}$‰) more likely prevailed.

Conclusions

1. While difficulties exist in interpreting the timing of Ab-horizon paleosols in badlands and prairie terrains, present studies suggest that they may serve as potential climate proxy indicators for climate change. Although individual paleosol distributions in time and space at project study localities cannot be correlated directly to each other, their stratigraphic regularity under suggested allocyclic conditions at Locality M, Elbee Bluff, and Douglas Creek indicates the utility of paleosols in climate studies.

2. The key to further work is in determining a way to obtain information from the unaltered material between soil horizons. This could include using textural, radiometric, and structural information to reconstruct the environment of deposition. The depositional environment would indicate whether rapid or slow deposition has occurred. Also, in cases where soils are located in a well-studied area, the mineralogic composition of the material can be used to identify its source area in an effort to determine rate and distance of transport, which should also provide information about the environment.

3. Localities such as badlands that are excessively geomorphically dynamic should be augmented from other environmental study localities, because the sedimentary records badlands preserve may mask more significant climate signals. Although these environments require more detailed work, they are still good candidates for short-term cycle study because there are highly sensitive to climate change.

4. Small-scale phenomena studies can identify periods of climate change. However, when separate locations are compared for the same time period, the indicated climates may not be identical. Factors such as differences in geomorphic processes, microclimates, and time delays are present in complex response relationships.

5. The climate model presented by Bluemle and Clayton[1] suggested Holocene time intervals of greater and lesser geomorphic stability (e.g., Wolf Creek Unstable Episode, Thompson Stable Episode). The temporal occurrence of most project paleosols within stable episodes supports their general climatic framework. In addition, the formation of Section M8302 – Unit 31 paleosol at the Douglas Creek Locality may correspond to a break in the Altithermal (maximum warming).

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[1] Bluemle, J.P., and Clayton, L., 1982, Geologic time in North Dakota: North Dakota Geological Survey Educational Series 14, 18 p.

6. The only evidence of significant C_4 vegetative input was from the uppermost parts of the Elbee Bluff and Douglas Creek Locality sections. Radiocarbon dates suggest that a change to drier and warmer conditions commenced at about 2700 YBP.

7. The stable carbon data support the following theory by Knox[2]: Hot, dry climates promote aggradation of material; cold, moist climates induce downcutting of stream channels and promote pedogenesis in other geomorphic settings. The stable carbon data on organic matter from the soil horizons indicate relatively cool and moist climates in every case but one.

Publications

Beck, D.L., and Hartman, J.H., 1997, Paleosols as proxy climatic change indicators in central North Dakota: North Dakota Academy of Science, Proceedings, v. 51, p. 161.

Hartman, J.H., 1997a, The ever-present chance of flooding, *in* Hartman, J.H., ed., Symposium on the Red River Flood of 1997 – Involving Science in Future Watershed Management Decisions: North Dakota Academy of Science (1997 Annual Meeting), Proceedings, v. 51, Supplement 1, p. 51–52.

Hartman, J.H., ed., 1997b, Symposium on the Red River Flood of 1997 – Involving Science in Future Watershed Management Decisions: North Dakota Academy of Science (1997 Annual Meeting), Proceedings, v. 51, Supplement 1, 52 p.

Hartman, J.H., Beck, D.L., Kuehn, D.D., Reid, J.R., and Reiten, J., 1997, Paleosols as proxy data for climate change—Interpreting Holocene deposits in the badlands and prairies of western North Dakota: Geological Society of America, Abstracts with Programs, v. 29, no. 6, p. A-34.

A paper by Beck and Hartman (1997) was given as a presentation by Ms. Beck. She competed in the Denison competition for best graduate student paper and was named runner-up. A Master's student, Ms. Beck was competing with Ph.D. candidate dissertation studies. Hartman (1997a) presented at a special symposium of the North Dakota Academy of Science at an annual meeting in response to the catastrophic flooding of the Red River of the North in April of that year. Dr. Hartman coordinated and edited the supplement issue resulting from this meeting (Hartman, 1997b). Hartman and others (1997) gave a poster at the annual meeting of the Geological Society of America in Salt Lake City, Utah.

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[2] Knox, J.C., 1984, Fluvial responses to small-scale climatic changes *in* Costa, J.E., and Fleisher, P.J., Developments and applications of geomorphology: Berlin, Springer-Verlag, p. 318–342.

Task 43 – Oxidation of North Dakota Scrubber Sludge for Soil Amendment and Production of Gypsum

Cooperative Power's Coal Creek Station has successfully marketed its fly ash for commercial use, and Cooperative Power has been an industry proponent of CCB utilization since Coal Creek Station became operational in 1981. With awareness of the economic and environmental advantages of byproduct utilization, the favorable EPA regulatory determination that CCBs are not hazardous, and the improved understanding of potential local and regional markets, Cooperative Power initiated an investigation on processing and utilization of Coal Creek Station scrubber sludge. Cooperative Power, the North Dakota Industrial Commission, and DOE provided funds for a research project at the EERC. The goals of the project were 1) to determine conditions for the conversion of scrubber sludge to gypsum simulating an ex situ process on the laboratory scale, 2) to determine the feasibility of scaleup of the process, 3) if warranted, to demonstrate the ex situ process for conversion on the pilot scale, and 4) to evaluate the quality and handling characteristics of the gypsum produced on the pilot scale.

The process development and demonstration phases of this project were successfully completed focusing on ex situ oxidation using air at low pH. The potential to produce a high-purity gypsum on a commercial scale is excellent. A relatively extensive evaluation of the pilot-scale flue gas desulfurization (FGD) gypsum product was performed to facilitate the marketing effort for this material in a broad range of applications, including agricultural uses. During the course of this evaluation, it was noted that some trace elements were present in measurable quantities in the FGD gypsum. These elements were mercury, chromium, and chlorine (present as chloride). Although they were present in measurable amounts, it is important to note that the mercury and chromium were present at very low levels, with leachate concentrations less than the primary drinking water standard levels. Air oxidation of scrubber sludge was carried out in laboratory- and pilot-scale operations. Initial experiments to provide information on efficiency of oxidation, most favorable reaction conditions (particularly pH), and other reaction variables such as air flow rates and the effects of iron and manganese catalysts were carried out in a five-necked 500-mL Pyrex reaction flask. The laboratory-scale experiments indicated that the reaction was rapid and complete and thus ideal for scaleup. The pilot-scale oxidation was carried out in a 500-gal stainless steel tank. All reaction conditions were maintained at optimum as determined in the laboratory studies with pH controlled to between 4.5 and 5.0 by adding 20% sulfuric acid as required.

The results of this project demonstrate the feasibility of converting Coal Creek Station scrubber sludge to gypsum exhibiting characteristics appropriate for agricultural application as soil amendment as well as for use in gypsum wallboard production. Gypsum of a purity of over 98% containing acceptable levels of potentially problematic constituents was produced in the laboratory and in a pilot-scale demonstration.

Task 44 – Pilot Plant Assessment of Fly Ash Agglomeration

The first few months of the project centered around finalizing a new design and orientation for the test furnace to accept the in-furnace ionizer and create adequate space for the “agglomeration chamber” downstream. Several meetings with Thermal Energy Systems, Inc. (TESI) representatives were held at the EERC to facilitate test furnace design changes and review ionizer design changes. These initial meetings focused mainly on the in-furnace ionizer. As a result of these discussions, changes to the physical orientation of the test furnace and construction of new system components were initiated. The furnace was moved physically in the pilot plant 1 ft to the south and was raised 1 ft to provide adequate space for access and ionizer controls. The redesign of the test furnace also involved adding a 3-ft refractory-lined section to the radiant zone to increase residence time in the furnace proper. In addition, the top section of the test furnace (where flue gases transition from vertical to horizontal flow) was redesigned to accept the graphite ionization rod and electrically isolate it from the test furnace. This section was refractory-lined to protect the metal shell from the hot flue gases and water-cooled to minimize the electrical conductivity of the refractory. The decking surrounding the furnace was reconstructed to accommodate these changes.

To evaluate the effectiveness of the in-furnace ionizer, a series of refractory-lined heat exchangers was constructed to both cool the gas stream for back-end temperature control and provide sampling ports that would allow measurement of the fly ash particle-size distribution as a function of residence time downstream of the ionizer. The combustion system also utilized water-jacketed heat exchangers for temperature control entering the ESP. To prevent the potential loss of naturally occurring SO_3 (a fly ash conditioning agent) by condensation on the cold wall of these heat exchangers, the flue gas cooling system was converted from water to air, raising the metal temperature above the dew point of the SO_3. The change to air was also accomplished to provide finer control of temperature to the downstream bipolar agglomeration chamber. Because air is a considerably less efficient cooling medium, additional surface was required to maintain temperature control within normal operating limits for an ESP. Two tube- and-shell heat exchangers were designed, contructed, and installed to provide the additional surface area required. The system’s forced-draft fan was relocated so that combustion air could be used to cool these heat exchangers, which became the first stage of the combustion air preheat system. A second forced-draft fan (existing on-site) was installed to provide cooling air to the remaining heat exchangers.

The combustion system layout included an ESP and a pulse-jet baghouse. The pulse-jet baghouse was removed to provide room for installation of the bipolar agglomeration chamber. The ESP normally associated with this system could handle approximately one-third of the total flue gas volume when particulate control was being assessed, with the remaining two-thirds of this stream bypassed to a cyclone. To meet the goals of this project, an existing ESP that could handle the entire flow from the combustion system was installed at the back end of the combustion train. A few days of shakedown testing of the new system components were performed to verify fan capacity and system viability.

The tasks described above were all completed prior to the work stoppage that was issued in response to non-payment by the commercial sponsor, Thermal Energy Systems, Inc. One major piece of equipment was purchased for this project, an aerodynamic particle sizer (APS) and some auxiliary equipment at a cost of approximately $45,500. The remaining project expenses were all related to the design, construction, and installation activities described above. The ionizers, power supplies, and control systems were to be provided by TESI. The EERC did not take delivery of any of these components, therefore, no testing of these systems was performed.

Task 45 – Small-Scale Demonstration of the Freeze–Thaw/Evaporation (FTE®) Process to Treat Oil and Gas Produced Waters

Evaporation ponds are used for produced water disposal in arid climates of the United States and Canada. Low construction and operating costs make them an attractive choice for natural gas producers. They are limited however, because they are effective only when seasonal temperatures and climactic conditions promote evaporation.

The Freeze–Thaw/Evaporation (FTE®) process addresses the problem of seasonal usage by coupling evaporation with freezing, which offers operators a year-round method for treating produced water. Treating water with the FTE® process reduces the volume of water to be disposed of as well as purifying the water to a level acceptable for watering livestock and agricultural lands. Coupling the natural processes of freezing and evaporation makes the FTE® process a more cost-effective and efficient method for the treatment and disposal of produced water. This process is currently used at evaporation facilities in the San Juan Basin in New Mexico and in the Green River Basin in Wyoming.

The basic concept is simple. Constituents in produced water lower the freezing point below that of pure water. When such a solution is cooled below 32°F, relatively pure ice crystals form, along with an unfrozen brine solution that contains elevated concentrations of salts. Because of the brine's high concentration of these constituents, its density is greater than that of the ice, and the purified ice and brine are easily separated.

The FTE® process operates in the following manner: When the ambient temperature drops below 32°F, produced water is automatically pumped from a holding pond and sprayed onto a freezing pad. The freezing pad consists of an elevated framework of piping with regularly placed, upright, extendable spray heads similar to those used to irrigate lawns. As the spray freezes, an ice pile forms over the elevated framework of pipes, and the brine, with an elevated constituent concentration, drains from the ice pile. The high-salinity brine, identified by its high electrical conductivity, is separated using automatic valves and pumped to a pond where it can subsequently be disposed of by conventional methods. As the ice pile increases in height, the sprayers are extended. When the ice on the freezing pad melts, the relatively pure water is pumped from the freezing pad and discharged or stored for later use. No new wastes are generated by the FTE® process.

San Juan Basin

Research sponsored by the Amoco Production Company, GRI, and DOE has been conducted since 1992 to develop a commercial FTE® purification process for produced waters. Numeric process and economic modeling, as well as the laboratory-scale process simulation that confirmed the technical and economic feasibility of the process, were performed by B.C. Technologies, Ltd., and the University of North Dakota EERC from 1992 to 1995. They then conducted a field evaluation from 1995 to 1997 in New Mexico's San Juan Basin at a conventional evaporation facility operated by Amoco Production Company. The results of this evaluation confirmed that the FTE® process has significant commercial economic potential. A new facility was designed in 1998, and its construction is expected to begin in 1999.

Green River Basin

B.C. Technologies, Ltd., the EERC, and GRI are currently involved in a commercial deployment at the Jonah field in the Green River Basin in southwestern Wyoming. In February 1998, the Wyoming Oil and Gas Conservation Commission approved the FTE® operation, and within weeks, freezing pads and spray equipment were added to the existing evaporation facility operated by McMurry Oil Company.

The commercial deployment operation of the FTE® process began at the end of February 1998. While the late start date and warm spring severely limited throughput to the freezing process, the FTE® plant was successfully operated at temperatures below −20°F, and treated water of a quality suitable for beneficial uses was produced. This was encouraging, considering a positive net production of ice was possible for only 2 weeks of operation, climatic conditions did not allow for aging of the ice pile, and the feedwater was predominantly from the “frac flow-back,” which is more difficult to treat than conventional produced water.

Following the ice melt, the FTE® facility operated in the evaporation mode. In spite of an unusually wet summer, a net 23,500 barrels of water was evaporated. Two additional brine ponds were added to the project in November 1998, and an FTE® deployment freezing operation began in December 1998 that will continue through the winter. The creation of two ice piles in excess of 40 feet in height is expected.

The current cost of disposal at this field when the FTE® process is utilized is approximately $1/bbl. Commercial facilities in southwestern Wyoming are charging as much as $6/bbl for produced water disposal. The cost of disposal varies according to disposal fees, which are generally used to maintain the facility, and the distance required to transport the produced water from the production site to the disposal facility. Weather conditions also contribute to the cost of transportation.

The FTE® process has a definite economic advantage over conventional evaporation technology in climates with seasonal subfreezing ambient temperatures. Since the process requires essentially the same equipment as conventional evaporation, it allows more water to be processed in an evaporation facility by operating at times of the year when evaporation is ineffective.

Technically feasible and capable of processing high-quality water suitable for the wide variety of beneficial uses cited previously, the FTE® process could also be applied to treating oil and gas residuals found at refinery or gas treatment plants and bases and to wastewater generated at food-processing plants.

Task 46 – Training and Support for Hot-Gas Filter Testing

The EERC conducted a 139-hour test to demonstrate acceptable performance of hot-gas filter elements in a pilot-scale system prior to long-term demonstration tests. The test was funded under DOE–EERC Cooperative Agreement No. DE-FC21-93MC30097, Task 3.13. In addition to the base program, the TRDU operation and filter element tests is benefitting other ongoing projects at the EERC. Sampling and analysis activities were completed in order to generate HAP data concerning trace metal transformation, speciation of mercury, and metal concentrations at selected points within the TRDU system in support of a project entitled “Trace Element Emissions” funded by the DOE Morgantown Energy Technology Center (METC, now the Federal Energy Technology Center, FETC). In addition, materials and ash data concerning high-temperature filter media and ash interactions were collected in support of a project entitled “Hot-Gas Filter Ash Characterization” jointly funded by FETC and EPRI.

The purpose of the work was to provide support and training for the vendors supplying the filter elements for the Wilsonville facility and for the DOE Clean Coal Program. The support activities included assisting vendors witnessing the test in obtaining photos, samples, and hard data documenting the test; expanded reporting and report distribution (after clearance from DOE); and press release(s) providing an independent third-party endorsement of filter performance. Training activities on start-up, operation, and troubleshooting provided direct benefit to the operation of the Wilsonville facility. In addition, the scope of the Base Cooperative Agreement (Task 3.13) was expanded to include four different filter types, rather than three.

The work conducted was sponsored with matching funds from Industrial Filter & Pump (IF&P), 3M Company, and Pall Advanced Filters.

The activities that were performed as a part of this proposed work include the following:

- Facilitating vendors in witnessing the test
- Obtaining photos, samples, and hard data documenting the test
- Expanded reporting and report distribution
- Press release(s) providing an independent third-party endorsement of filter performance
- Training activities on start-up, operation, and troubleshooting
- Testing four different filter types, rather than three

The scope of work was conducted in two distinct time periods. The first effort was undertaken during the installation of the filters, start-up and operation of the TRDU and hot-gas filters, shutdown of the unit, and removal of the filters for inspection. Representatives from the 3M Company were present during the installation of the 3M filters. A representative from the M.W. Kellogg company was present during the operation of the TRDU in support of the Piñon Pine Clean Coal Project. Representatives from DOE, Westinghouse, and 3M were on-site to examine the filters after the test was completed. Numerous photos were taken of the TRDU and hot-gas filter elements.

The photos and data were presented at three project review meetings and two conferences:

EERC – Hot-Gas Filter Workshop
Date: April 30, 1996

Southern Company Services, Inc. (Savannah, Georgia)
Date: May 6–9, 1996

METC – EM Review Meeting
Date: June 3–6, 1996

METC Contractor's Conference
Date: July 16–18, 1996

Pittsburgh Coal Conference
Date: September 3–5, 1996

The program also allowed for additional training and shakedown of the new Genesis software control package and the hot-gas filter backpulse and letdown systems. Originally, there were three candle filter types to be used in the test program: 3M, Pall Iron Aluminide, and IF&P. A fourth type was added: Pall Vitropore.

Operational data from the test program have been provided to FETC in Lotus spreadsheet format.

Task 47 – Development of a Coal Combustion Byproducts (CCBs) Database System

Nearly 90 million tons of coal combustion products (CCPs) are produced annually in the United States. The value of CCPs is well established by research and commercial practice; however, only 25% of these products are utilized. The 1994 U.S. Department of Energy report to Congress, *Barriers to the Increased Utilization of Coal Combustion/Desulfurization Byproducts by Governmental and Commercial Sectors* (DOE Office of Fossil Energy), states that there are several major areas of institutional barriers to utilization. Two of these areas are 1) inadequate information, including both engineering and environmental data and 2) inefficient technology/information transfer to CCP producers, end users, regulators, or potential users of CCP technology.

The American Coal Ash Association, dedicated to advancing the technically sound, commercially competitive, and environmentally safe use of CCPs, is striving to remove these barriers. CCPs commonly include fly ash, bottom ash, and boiler slag. These materials may vary widely by material type, coal feedstock, combustion conditions, collection systems, and other operational parameters. The characterization of CCPs provides valuable information relevant to the use of the materials. The ability to compare the material characterization on the basis of engineering and analytical data is beneficial in decisions related to CCP utilization.

The objective of this project was to develop a computer program containing a database of advanced analytical and comprehensive engineering information on CCPs, accessible through a user-friendly interface. Version 1.0 of the *ACAA CCP Data Manager* was specifically designed to:

- Perform multiple-criteria queries to produce a set of samples for in-depth study.
- View and print standard test reports, such as C 618 reports.
- Compare and contrast analytical results in graphs and tables.
- Graph utilization information by application and region.
- Save data to a file for use in other computer applications, such as spreadsheet programs.

The program was designed to contain descriptive information about a given CCP sample, including sample formation data (material type, sample location, fuel type, collection device etc.), combustion system design data (steam generator type, furnace type, SO_2 and NO_x control information, ash-handling configurations), test data (chemical, mineralogical, and physical characterization data), and utilization potential of the CCP. The location of the plant is identified by region. The database has been initially populated with information on over 800 CCP samples taken from the Coal Ash Resources Research Consortium (CARRC). An installation package and user's guide was developed for unlimited distribution by the ACAA.

The main features of the program are *Query, Select, View, Report,* and *Graph*. *Query* provides a way to reduce the database to a set of samples matching specific criteria, for example, “retrieve all samples where the material type is fly ash and the utilization potential is cement and concrete products and the samples were produced in Region 1.” *Select* allows the user to further narrow the query by selecting specific samples returned from the query. *View* displays all of the available information on the samples. *Report* provides a variety of reports to view and print, including laboratory reports, C 618 reports, and utilization reports. *Graph* provides a menu of predefined graphs to choose from, such as comparing test results of selected samples or displaying the total number of samples identified for selected utilization potential within each region.

The program has applications for a variety of users, including CCP producers, marketers, and researchers. CCP producers can compare CCPs produced at their plant(s) with CCPs produced under similar conditions at other plants. Producers can use the program to plan for changes in fuel sources or other physical changes in the plant that will affect the quality of their ash. Marketers will be able to examine product consistency over a period of time. CCP producers and marketers can compare CCP properties and elucidate new ways to utilize a particular CCP. Researchers can use the program to identify CCPs that may be specified for emerging technologies. Researchers could also use the program to study how production condition interactions affect the characterization of CCPs.

Task 48 – Coal Ash Behavior in Reducing Environments (CABRE) II

Accomplishments during the first and second years of work in the CABRE II program are outlined below by task.

Task 1 – Ash Formation, Year 1

Work has progressed this year to optimize operation of the pressurized entrained-flow gasification (PEFG) simulator. Shakedown experiments were conducted to optimize start-up procedures (e.g., pressurizing the system with the staged gas burner on), operability of the staged gas burner, temperature control, operation of the coal-feeding system, and safety procedures. To optimize experimental methods, tests were conducted in an atmospheric entrained-flow gasification and combustion (AEFGC) simulator. These tests resulted in improved procedures for 1) gas burner operation, 2) determination of operating conditions (in particular axial temperature and gas concentration profile measurements), 3) control of deposit plate temperatures, and 4) ash formation and deposition experiments.

Scanning electron microscopy was used to discern the morphology of char and ash and deposited materials produced in the AEFGC simulator. The deposited ash clearly showed the formation of a small deposit initiation layer consisting of very small particulate matter, possibly constituting condensed vapor species. Additions of doped gaseous components in the test systems were clearly reflected in considerable levels of the solid condensed particulate in the deposit with compositions similar to the dopants.

Also within Task 1, several coals were selected by the sponsors as test coals for this program: 1) Illinois No. 6, 2) Puertollano, 3) SUFCo, 4) Drayton, 5) Wyodak, 6) El Cerrejon, and 7) Skyline. Skyline and Puertollano coals were analyzed at the EERC for hydrogen, nitrogen, fixed carbon, sulfur, oxygen, total ash content, major elemental oxides, and coal minerals. The Puertollano coal is relatively high in calcium, low in iron, moderately high in sulfur, and very high in ash. The Skyline coal is moderately high in calcium, sodium, and silicon. Both of these coals are bituminous in rank.

Task 1 – Ash Formation, Year 2

A PEFG simulator was designed and constructed to enable a laboratory-scale simulation of the fate of coal particles and their mineral matter content in (dry-feed) PEFG systems. Work has progressed this year to optimize operation of the PEFG simulator. Shakedown experiments were completed to optimize start-up procedures (e.g., pressurizing the system with the staged gas burner on), staged gas burner performance, temperature control, coal feeder system, particulate collection, and safety systems.

The inner burner of the PEFG simulator is fired with an oxygen-rich gas mixture, which may contain methane, carbon monoxide, carbon dioxide, nitrogen, and hydrogen sulfide, to simulate the oxidizing conditions of the near-burner zone in the gasifier. Coal, char, or ash particles are fed through the inner burner and undergo rapid heating (heating rate $>10^5$°C/s) up to the high-temperature level of the near-burner zone (>2000°C, the high temperature being created by the gas flame). The particles are fed at a typical rate of 1–5 g/h by means of a commercial rotating brush feeder. The assembly of coal feeder, gas burner, reactor tube, and heating sections is housed in a pressure vessel enabling operating pressures of ≤2 mPa.

The inner burner is surrounded by an outer burner, which is fired under substoichiometric conditions, resulting in a strongly reducing, relatively low-temperature flame. The gas mixture may consist of oxygen, methane, carbon monoxide, and hydrogen. Along the vertical axis of the reactor, slow mixing of the gases occurs from the inner and outer burner, which causes the gaseous environment for the particles falling in the center of the reactor to change from oxidizing to strongly reducing. Simultaneously, the particle temperature decreases from >2000°C (simulating the near-burner zone) to 1400°–1600°C, simulating the downstream reducing zone, or even down to 600°–800°C to simulate gasifier operation with a gas quench.

Particle sampling between residence times of 10 ms to approximately 1 second is possible with a fast quenching probe in combination with a cyclone and/or a filter. Alternatively, a deposition probe may be used for slagging and fouling tests. In addition to the particle sampling, optical access ports are available at five different axial positions for in situ measurement of temperatures, particle sizes, and velocities.

Shakedown testing work has shown: 1) satisfactory performance of the control and safety system; 2) stable performance of the staged gas burner, including a tertiary ring for extra CO and H_2 supply at pressures of ≤1 mPa; 3) satisfactory furnace temperature control up to 1000 °C, with an effective suppression of convective heat fluxes; 4) adequate particle feeding; and 5) adequate particle collection using the oil-cooled collection probe in combination with a cyclone and a filter. A procedure has now been developed by which stable operation at 10 bar can be reached within 40 min. PEFG simulator experiments are producing gasification fly ash and deposit samples for characterization.

Also within Task 1, the following coals were characterized for this program: Illinois No. 6, Puertollano, SUFCo, El Cerrejon, and Skyline. Analysis results are also available on a Wyodak coal, which is not being tested in CABRE II, but was used in as a test coal for gasification testing under another project at the EERC. An additional coal, Drayton, has yet to be supplied for analysis, but it will be acquired from KEMA and analyzed.

Task 2 – Ash Deposition, Year 1

Open discussions with individual sponsors were held so that information generated in this program can directly apply to sponsor systems. During the first 8 months of the program, each commercial sponsor had an opportunity to visit with EERC and ECN project leaders. Several system deposit samples were received from individual sponsors, and the analysis results, when completed, will be used in adjusting test procedures and validating modeling work.

Fly ash was collected from a large-scale gasifier that was firing one of the sponsor-selected fuels, along with a fluxing agent additive. SEM micrographs showed mineral particles as completely molten spheres of calcium aluminosilicate/sulfate material and larger residual char particles, with certain of the larger char particles having very porous morphologies. Comparisons were made between the ash collected from the full-scale gasifier unit and ash generated in the

AEFGC-simulator at ECN, which was firing the same fuel. These types of comparisons between systems will continue to be very important for this project to help fine-tune the smaller experimental systems.

Work has progressed in Task 2 to note the impacts of two different gas conditions on slag viscosity: highly reducing and lower reducing conditions. More specifically, the variation in slag viscosity with the change of both H_2O/H_2 and CO_2/CO composition in fuel gas was investigated. Two coals were tested in this task, with slags being produced using ASTM procedures involving the ashing of the coals. Coal A ash slag showed lower viscosity relationships than Coal B slag, possibly because of the fluxing action of the more abundant calcium with aluminosilicate material and considering that the similarly low quantities of iron in both coals are not impacting the viscosity too greatly. Activation energy of viscous flow in the Newtonian range is greater for the Coal B slag, which indicates stronger attractive forces between cations and oxygen ions in the aluminosilicate structures as a result of the lower alkali and alkaline-earth element content.

Gas compositions were varied in degree of reducing components, specifically the amounts of CO_2, CO, and N_2 in the gas environment used during the rotating bob viscometer tests on the slags. Differences in slag viscosity under the low and high reducing conditions proved to be negligible for Coal A. The effect of water vapor on the slag viscosity of Coal A was also negligible. As additional results are acquired for more coal slags and conditions, a more in-depth interpretation will be put forth for the impacts of reducing gas composition on viscosity.

Initial steps have been taken to outline an approach for devising an improved viscosity prediction model for gasification ash and slag. The model will be applied more toward cooler heat exchange regions or transition regions between the slagging reactor and heat exchangers in an entrained-flow gasifier. A modified Urbain predictive viscosity model that has been used extensively at the EERC for predicting liquid-phase viscosity of melt systems formed from combustion coal ash has been selected for modifications to improve its applicability to materials associated with gasification environments. The model is based on the principles of heat capacity calculations related to temperature and chemistry. Providing a complete description of slag rheology to improve the Urbain type of slag viscosity model requires the study of viscous flow, both in Newtonian and non-Newtonian regions. Non-Newtonian behavior can be represented by Bingham plastic melts, which are well evidenced in colloidal suspensions. In an attempt to devise an appropriate slag model for gasification systems, the Newtonian range of viscous flow, which extends up to the critical temperature, T_{cr}, at which the phase transformation may occur, and the non-Newtonian ranges of viscosity will need to be joined.

Also in Task 2, progress has been made to characterize low-temperature deposit strengths. The diametral compression unit for measuring the strength of experimentally generated low-temperature deposits was fabricated at the EERC. It utilizes a load cell, a data acquisition system, and an inchworm drive mounted on a framework, and future tests will focus on how different gas environments, temperatures, and ash compositions affect pellet strength.

Task 2 – Ash Deposition, Year 2

The experimental work in ash deposit formation and development is planned for the end of Year 3 of the project, following the ash formation experiments (Task 1).

Several deposit samples were received from Babcock–Hitachi, K.K., that were collected from their HYCOL gasifier. The samples were produced from gasifying a Taiheiyo coal. Slag deposits from the gasifier are characterized by relatively large (<100 µm in longest dimension) plagioclase ($[Na,Ca][Si, Al]_4O_8$) phenocryts rimmed with tiny (<2 µm in diameter) dendritic spinel ($[Fe^{2+}, Mg, Ti]\ [Al, Cr^{3+}, Fe^{3+}]_2O_4$) crystals in a glass matrix. These slag microtextures are very similar to those documented for the slag samples produced experimentally, suggesting that gasification conditions are being simulated.

Experimental work has nearly been completed in Task 2 specific to investigations of coal ash type and reducing gas conditions on slag viscosity. More specifically, the variations in slag viscosity with the change of both H_2O/H_2 and CO_2/CO composition in fuel gas have been investigated for several coals, including Illinois No. 6, SUFCo, El Cerrejon, Skyline, and Puertollano coals. Some of the tests involved using calcium modifiers to note their impact on slag viscosity. The following relationships regarding slag viscosity were determined experimentally:

- Water vapor and hydrogen sulfide gases do not significantly change the viscosity of ash slags under reducing conditions.

- Lowering viscosity by adding CaO increases the propensity of iron ions in Illinois No. 6 slag to reduce to metallic iron under the same reduction conditions.

- Iron oxide added into a slag reduces the viscosity of the slag and does not cause a significant increase in viscosity at the critical temperature, as the addition of calcium oxide does.

- Oxygen fugacity in gases used for viscosity tests is about 10^{-9} atm.

Also within Task 2, major strides have been made in determining the mechanisms of gasification deposit strength development at lower temperatures. An approach for generating ash pellets and measuring strength during low-temperature sintering in a gasification environment was devised. Essentially, coals are ashed and the ash is slagged, crushed, sieved, and made into a pellet that is subjected to a reducing environment. Crushing strengths are then determined on several pellets derived from the same coal ash and averaged. The experimental procedure was checked against cyclone ash from the Krupp Uhde Fürstenhausen plant. Several tests have been performed, and preliminary results have been assembled. The following relationships regarding ash sintering were identified experimentally:

- Sulfidation of ashes under gasification conditions causes separation of sulfides from silicates if the concentration of sulfur in silicate is above chemical equilibrium.

- Precipitates of sulfide phases at the particle–particle interface as well as enlarged potassium content cause an increase of the deposit strength.

- Chemical transport reactions activated by hydrochloric gas and water vapor are a potential source for low-temperature sintering of ashes.

Task 3 – Index Development and Demonstration, Year 1

Thus far, a design shell and graphical user interface for how the predictive model will function have been formulated. The prediction of the fine ash particles in the model will be driven largely by the ability to accurately predict the vapor species derived from the inorganic components. Modifications to the inorganic components that will be vaporized during the initial gasification process will be determined by a commercially available thermodynamic equilibrium code. These vapor species will affect the existing mineral coalescence, vaporization, and condensation mechanisms in the model. This portion of the model has nearly been completed. A shell of a user interface has been formulated, which includes the selection of a gasification temperature, an area of interest temperature, boiler pressure, coal feed rate, air feed rate, and steam feed rate, followed by the calculation of deposit chemistries and buildup rates in different regions of a gasification system.

Task 3 – Index Development and Demonstration, Year 2

A design shell and graphical user interface for the predictive model function have been formulated that include the selection of a gasification temperature, an area of interest temperature, boiler pressure, coal feed rate, air feed rate, and steam feed rate, followed by the calculation of deposit chemistries and buildup rates in different regions of a gasification system. Currently, temperatures used to predict entrained particle-size and composition distributions (PSCDs) and vapor species apply to only one region in the gasifier. Ash deposit chemistry and buildup rates are then derived from the PSCD and vapor data. Future versions of the model will allow several gasifier regions and temperatures of interest to be selected, the addition of a heat exchanger, and the selection of an air pollution collection device. Near the end of Year 2, gasification simulation tests on the PEFG simulator and viscosity determinations at the bench scale have provided some of the necessary data to enhance existing ash transformation codes, and the modeling work will be accelerated.

Task 4 – Management and Reporting, Year 1

A kickoff meeting was held at the beginning of the project in May 1996 at ECN in Petten, Netherlands. Represented at the meeting were all of the project participants and sponsors, including the EERC, ECN, KEMA, Elcogas, Krupp Uhde, Babcock–Hitachi, K.K., Novem, and EPRI. The project work plan was thoroughly presented, and project budgets and milestones were discussed in detail. Sponsors were encouraged to provide deposit and ash samples from their respective operating units. An interim meeting was held at the EERC in Grand Forks, North Dakota, in October 1996, with all of the sponsoring agencies in attendance except DOE. At the meeting, the work plan was finalized, and progress in analyzing sponsor deposit samples and work on the ECN PEFG simulator were presented. An interim Year 1 report was sent out to all CABRE II participants in August 1997, and a Year 2 semiannual meeting was held October 9 at EPRI headquarters in Palo Alto, California.

Task 4 – Management and Reporting, Year 2

A Year 2 project review meeting was held on May 28, 1998, at ECN in Petten, the Netherlands. Progress to date on project work tasks were thoroughly presented. Project budgets and milestones were also discussed in detail. A draft Year 2 final report was issued May 28 for all CABRE II participants to review. A revised Year 2 final report was issued June 30 to all CABRE II participants.

Task 49 – Validation of Fireside Performance Indices

The Validation of Fireside Performance Indices project was formulated with the goal of validating and improving the predictive ability of the PCQUEST (Predictive Coal Quality Effects Screening Tool) Program developed at the EERC under the previous Fireside Performance Indices project through advanced analysis methods, bench-scale combustion testing, and comparison with full-scale utility boiler experience. At the same time, the project was designed to assist commercial sponsors in the resolution of specific coal quality and ash deposition issues. The project will continue under the new DOE Cooperative Agreement No. DE-FC26-98FT40320.

Fifteen subprojects involving ten different commercial sponsors were completed, with one project being carried into the next Cooperative Agreement. The project has been quite successful, broadening the database of detailed analyses, particularly of eastern bituminous coals; providing bench- and full-scale information being used to validate the fireside performance predictions; providing additional insight on the effects of operating conditions and temperature on fouling and slagging behavior; and providing the basis for valuable improvements in the PCQUEST software to take into account furnace exit gas temperature changes and perform effectively with biomass fuels.

Task 50 – Deposition of Lignites in the Fort Union Group and Related Strata of the Northern Great Plains

With the aid of a grant from the Philip M. McKenna Foundation and joint venture funding from DOE, Late Cretaceous, Paleocene, and early Eocene geologic and paleontologic studies were undertaken in western North Dakota, eastern and south-central Montana, and northwestern and northeastern Wyoming. These study areas comprise the Williston, Bighorn, and Powder River Basins, all of which contain significant lignite resources. Research was undertaken in these basins because they have the best geologic sections and fossil record for the development of a chronostratigraphic (time–rock) framework for the correlation of lignite beds and other economic resources. A thorough understanding of the precise geologic age of the deposition of sediments permits a powerful means of interpreting the record of geologic events across the northern Great Plains. Such an understanding allows for rigorous interpretation of paleoenvironments and estimates of resource potential and quality in this area of economically significant deposits.

This work is part of ongoing research to document change in the composition of molluscan fossil faunas to provide a paleoenvironmentally sensitive independent means of interpreting time intervals of brief duration during the Late Cretaceous, Paleocene, and Eocene. This study focuses on the record of mollusks and, to a lesser extent, mammals in the 1) Hell Creek–Tullock Formations, which include the Cretaceous–Paleocene boundary, in the western portion of the Williston Basin, Montana; 2) uppermost Cretaceous, Paleocene, and lowermost Eocene strata in western North Dakota, which includes the last interior seaway in North Dakota; 3) upper Paleocene and lowermost Eocene of the northern portion of the Bighorn Basin of south-central Montana and northwestern Wyoming; and 4) Powder River Basin of northeastern Wyoming and southeastern Montana. The geologic record in each area provides different physical and paleontological information to aid in interpreting the geologic record through the study interval. The results of these efforts have been published or submitted for publication. The following paragraphs summarize the biostratigraphic results in the study areas.

Western Williston Basin (Montana)—Latest Cretaceous–Earliest Paleocene

The record of freshwater bivalves (Unionidae) through the Latest Cretaceous (K) and earliest Tertiary (T) (early Paleocene) is marked by times of high and low diversity. The change in diversity appears coincidentally at or just below the K/T boundary. Where best documented in the northern plains of Montana, particularly in the stratotype of the Hell Creek Formation in the western portion of the Williston Basin, freshwater mollusks are abundant in fluvial channel systems. In uppermost Cretaceous strata, molluscan faunules are generally dominated by freshwater bivalves, including thick-shelled clams of both simple (*Plesielliptio, Rhabdotophorus*) and complex surface sculpture, and nonovate shell shapes (*Proparreysia*, *Plethobasus*, *Pleurobema*). Apparently, as in the distribution of dinosaurs, highly sculptured and/or trigonally shaped unionids range abundantly throughout the Hell Creek Formation but are absent in strata within a few meters or less of the K/T boundary. Throughout the Williston Basin and elsewhere in the Western Interior, Paleocene freshwater bivalves and nonmarine mollusks in general have been found, but at only a few localities that contain depauperate faunules. The only unionids found to date in the Tullock or Ludlow Formations of the Fort Union Group are ovate–elongate in shape and are simply sculptured with concentric (nonchevron) umbonal corrugations (*Plesielliptio*) or dorsal postumbonal dorsally directed curvilinear ridges (*Rhabdotophorus*) or are without sculpture ("*Unio*"). This dramatic faunal change and the reduction in general abundance were long-lasting. Freshwater bivalve localities remained relatively uncommon for at least four million years (late middle Paleocene, late Torrejonian). Simple sculpture and shell form persisted throughout the Paleocene and into the Eocene, and unionid diversity remained low. What molluscan record exists just below the boundary suggests a Paleocene faunal composition, but these occurrences are rare and possibly environmentally influenced. This history of unionids is presently not ascribable to a K/T event.

Williston Basin (North Dakota)—Latest Cretaceous–Earliest Eocene

The uppermost Cretaceous and Lower Tertiary (Paleocene–Eocene) strata of the North Dakota portion of the Williston Basin contain significant geologic sections, including 1) the type area of the Fort Union Group, 2) the most complete record of the Cannonball Formation, and 3) the youngest Cretaceous (Fox Hills and Breien) and oldest Tertiary (Cannonball) marine strata in the interior of North America. Present studies have correlated these strata to the North American Land Mammal Age biochronology and a current radiometric and polarity chronology. On the basis of palynomorphs, the Hell Creek–Ludlow formational contact is effectively isochronous and a near match to the K/T boundary across western North Dakota. Planktic forams from the main body of the Cannonball Formation indicate the unit as lower but not basal Paleocene. The Cannonball Formation is correlated to a radiometric timescale on the basis of current planktonic foram zone age dates. Three tongues of the Cannonball Formation have been recognized. Radiometric dates and mammalian fossils suggest a Puercan age for the lowermost tongue, while the Boyce and Three V Tongues are probably of Torrejonian (To) age. The diachronous nature of the Slope Formation appears to be confirmed by a radiometric date near the base of the Bullion Creek Formation and the middle Tiffanian (Ti3) Brisbane mammalian local fauna. The Bullion Creek–Sentinel Butte formational contact is temporally well controlled on the basis of a number of low-diversity mammalian local faunas. Fort Union strata, as examined by F.V. Hayden in the middle 1800s, can now be restricted to the Ti3 and Ti4 ages. The age of the Sentinel Butte–Golden Valley formational contact is not well controlled. Floral similarities between the Bear Den Member and the Fort Union southeast of Red Lodge, Montana, suggest an early Clarkforkian age for the lower part of the Golden Valley Formation in North Dakota. The mammals, mollusks, and flora of the Camels Butte Member indicate a Wasatchian (Wa) age. The mammals from the White Butte Locality further suggest the Wa3 biochron.

Bighorn Basin (Wyoming–Montana)—Late Paleocene–Early Paleocene

The nonmarine molluscan fauna in the Western Interior of the United States underwent large-scale changes during the time represented by the Laramide Orogeny. This period began with the loss of many bivalve and gastropod taxa near the Cretaceous–Paleogene boundary, followed by an increase in mesogastropod diversity in the late Torrejonian and Tiffanian, then a reduction in such diversity into the Clarkforkian that is associated with a dramatic increase in the representation of terrestrial prosobranch and pulmonate families prior to the beginning of the Wasatchian age. The latter portion of this record is well documented in the northern portion of the Bighorn Basin in Wyoming and Montana. The Clarkforkian–Wasatchian boundary, equated by some with the Paleocene–Eocene boundary on the basis of the pattern of mammalian evolution and other evidence in this area, is delimited by aquatic and terrestrial mollusks, but the faunal change is less dramatic in the Bighorn Basin than changes associated with the increase in terrestrial taxa during the middle Clarkforkian. However, certain nonmarine molluscan taxa appear to be good indicators of an early Wasatchian age, whether they occur in the San Juan Basin of New Mexico or on the Wasatch Plateau of Utah. The present study shows that molluscan taxa appear capable of indicating Clarkforkian biochrons in the absence of mammalian fossils in the Powder River Basin of southeastern Montana and northeastern Wyoming. The approximate stratigraphic horizon of the early and middle Clarkforkian boundary is near the level of the Anderson coal bed, while Wasatchian-age strata occur just above the Arvada coal bed in the main body of the “Wasatch” Formation. The boundary is documented by both the loss and introduction of different species of mesogastropods and aquatic pulmonates, as well as a few species of unionid and pisidiid bivalves. The Clarkforkian–Wasatchian boundary in the Willwood Formation of the Clarks Fork Basin can be determined on the basis of these taxa and also by a well-differentiated and diverse terrestrial snail fauna.

Task 51 – Oxygen Plasma Unit for Soil Decontamination: Demonstration of a Field-Scale Unit

EN-DYN, Inc. (now AGSCO) and the EERC proposed to demonstrate the economic and technological feasibility of a field-scale oxygen plasma unit for the cleanup of soils contaminated with pesticides, petrochemicals, and other organic toxins. Previous projects at the EERC have demonstrated the use of low-temperature oxygen plasma (LTOP) to break down harmful organics into the basic constituents of carbon dioxide and water. To accomplish this objective, the program was divided into three tasks: Task 1 consisted of the design of a unit capable of processing 5 tons of contaminated soil per hour. The demonstration unit design consists of four major subsystems: the reactor and reactor bed support system, radio frequency power source and antenna array, product gas cleanup system, and high-vacuum system. Task 2 consisted of the construction and shakedown of the demonstration unit. Task 3 consisted of the demonstration of the oxygen plasma technology's ability to clean contaminated soil at a minimum of three field sites.

Prior to the completion of Task 1, the oxygen plasma prototype was operated to verify the ability to remediate toxaphene-contaminated soils. Preliminary testing yielded toxaphene removal efficiencies of only 65% and 70%. EN-DYN and the EERC made a decision to refocus effort on a testing program that would determine operating conditions that would result in 100% removal of the contaminant before proceeding with Task 2.

Thirty-three tests were performed by EN-DYN, Inc., personnel using the EERC 500 pound-capacity prototype to validate the remediation of toxaphene from a toxaphene–clay soil matrix. Four preliminary shakedown runs were performed to train EN-DYN, Inc., personnel on the prototype operation. A 20-run fractional factorial experimental matrix was then performed to evaluate the effects of radio frequency power level, oxygen flow rate, quantity of soil charged to the reactor, reaction pressure, and reaction time on the removal of contaminants from the soil. A validation run was then performed, resulting in a 70% removal efficiency. The remaining tests were performed following several equipment modifications designed to improve removal efficiencies. The results of the testing showed the prototype LTOP unit was unable to reproduce the consistently high removal efficiencies required to validate prototype operation for the remediation of toxaphene-contaminated soil.

On August 30, 1996, the EERC held an internal technical review of the oxygen plasma technology to discuss technical difficulties encountered during the toxaphene remediation program with its senior research staff. The review determined the oxygen plasma technology to have technical merit and to be based on sound engineering practices, but a more extensive characterization research program utilizing the prototype unit would be required before continuing the development of a commercial demonstration unit. A decision was made at this time to suspend development of the demonstration unit. EN-DYN, Inc., and the EERC are continuing to review the oxygen plasma technology and are exploring new opportunities to develop the necessary research and development program required to further characterize the process before proceeding with a commercial demonstration unit.

Task 52 – Evaluation of a Zirconium Additive for the Mitigation of Molten Ash Formation During Combustion of Residual Fuel Oil

Florida Power & Light Company (FP&L) was firing a residual fuel oil (RFO) containing catalyst fines, which resulted in a troublesome black aluminosilicate liquid phase that was freezing to a hard black glass and damaging the contracting waterwalls of the boiler. The EERC performed a series of tests for FP&L to evaluate the effectiveness of a zirconium additive to modify the mechanism that forms this liquid phase. The objective was to find an additive that would result in the formation of a dry refractory phase that could be easily handled during cleanup of the boiler.

Baseline testing of the RFO with $Mg(OH)_2$ addition was performed in two separate test combustors of different scales. The first of these tests covered 15 hr in the EERC combustion test facility (CTF). Two additional tests were performed in the conversion and environmental process simulator (CEPS) combustor, the first covering a 3-hr duration and the second covering a 12-hr duration using higher furnace and probe metal temperatures. Results for each indicated similar deposit formation. Very small drops of slag were formed at the surface in each of these tests; however, the slag formation was not as dramatic over this time period as was expected. Microscopic examination of each deposit confirmed the onset of slag formation. Because significant slag formation (visible to the naked eye) was not achieved in the 15-hr test period on the CTF or the 12-hr test period on the CEPS, an alternative work plan was sought and all work was suspended so that FP&L could review options.

Several options were considered to decrease the time or fuel required to form the baseline deposits. The first option was to run for an extended time period in the CTF (up to 48-hr durations), requiring additional fuel from FP&L. The second option was to add additional ash to the RFO to increase its ash concentration from 0.08% to 1.0%. A 5-gal sample of ash was obtained from FP&L's Riviera Plant dust collector and analyzed for this purpose. This sample consisted of only 11.4% ash. To increase the ash concentration of the oil to 1.0%, about 8 lb of material was required per 100 lb of oil. The third option was to perform the tests in the CEPS, which fires at a rate of less than 2 lb/hr, for an extended time period.

It was determined that formation of the baseline deposit is essential to the overall success of the project and that testing of the additive would be meaningless in the absence of an established baseline. Because project resources (both fuel and funding) were limited, FP&L requested that all project activities be suspended indefinitely.

To determine the effectiveness of zirconium as an additive for mitigation of the troublesome black glass, one or more of the recommendations below should be followed:

- Perform additional testing at the pilot scale over a test period of up to a 100-hr duration to establish the baseline deposit.

- Addition of fly ash may be used to accelerate deposit growth.

- Perform a series of pilot-scale tests using the additive, with the same test duration as that established during baseline testing. Additive ratios of 1:1, 2:1, and 3:1 should be tested.

- Perform a series of additive tests similar to the above at full scale, collecting deposits over various time intervals to establish the long-term effects of using the additive.

In the absence of pilot-scale test results, caution should be used during full-scale testing of the additive to prevent an irreversible deposition event.

Task 53 – Construction, Demonstration, and Evaluation of an Economic and Environmentally Safe Evaporation and Holding Pond Design

The EERC was to construct a prototype of a unique holding pond design, which would offer the following advantages:

- The pond can be constructed for 20% to 40% of the cost of a conventional pond with double synthetic liners.
- A surface-level gravel/sand pack with well screen header and seepage collection trench overlying compacted native materials virtually ensures no subsurface leakage.
- Subsurface leakage can be detected by the moisture sensor grid included in the design. This sensor grid can be used to confirm that subsurface leakage is zero.

Project objectives were to acquire regulatory approval for construction and demonstration of the pond; construct the pond with installed piping, pumps, and instrumentation; operate the pond to collect sufficient data for an evaluation; and evaluate the technical and economic regulatory feasibility of the design, and gain regulatory approval for further use.

Unfortunately, the commercial sponsor, EPRI, terminated the project before the pond was constructed. At that point, $21,259 of EPRI funds and $5600 of DOE funds had been used. Accomplishments to that point were as follows:

- A site had been selected by the Amoco Production Company.
- Specification of the leak detection system components was completed, and site characterization had been planned. After site characterization, site-specific details of the leak detection system could be finalized.

Task 54 – Advanced Carbon for Environmental Applications

Collection of HAPs from combustion gas streams is the focus of much current research nationally and internationally. An equally important aspect of dealing with HAPs from postcombustion cleanup of effluent (hot) gas streams is the disposal of the concentrate that accumulates in (on) sorbents and combustion residues during the collection process, which presents an underemphasized secondary HAP containment problem.

Current state-of-the-art control technologies rely heavily on activated carbons and wet scrubbers. The end market value of an activated carbon is currently $1/lb or $2000/ton. An active char with a price of $500 to $700/ton should have a market. Finding a process that will produce activated carbon from North Dakota lignite would be an economic boon to environmental cleanup activities. The objective of this project by the EERC was to determine whether super- or subcritical water extraction processing will effectively dry coal, extract tars, decrease ash content, and reduce inert volatile matter to produce a physically strong, higher-surface-area char that can be further processed to be an exceptional activated carbon. Further efforts would be required to determine processing details prior to commercialization.

The EERC and Environmental Energy Systems Incorporated (EESI) through a collaborative effort developed and tested a hydrothermal process involving principles of sub- and supercritical water processing for use in the production of activated carbon for environmental pollutant cleanup applications. Innovative technologies are needed to remediate the increasing volumes of waste materials. Various lignite and solid waste material were processed at subcritical conditions. The chemical material and the physical and chemical properties were evaluated for potential use as activated carbons. The initial results indicate hydrothermal treatment may not only be an effective method for production of char, but also as an extraction method to clean contaminated carbons used to remove contaminates from flue gas. Hydrothermal process removed over 90% of the mercury from contaminated activated carbon. Based on multigram testing performed during this project, EESI has prepared two proposals aimed at treating contaminated activated carbons and hydrothermal processing of coal and mixed waste for power generation.

Task 55 – Binderless Agglomeration of K-Fuel® Product Preliminary Evaluation

The goal of this project performed by the EERC was to evaluate the technical and economic potential for using binderless agglomeration to reconstitute K-Fuel®-treated low-rank coal to produce a premium fuel for industrial stokers, utility boilers, and domestic heating furnaces. It was contended that a combined process would yield a strong lump product that was stable toward water reabsorption, friability, and spontaneous or self-heating and that retains the desired properties of the K-Fuel®-treated coal. Furthermore, the combined process would provide a technology with significant export potential to East Central Europe and the Asia–Pacific region, where there are reserves of billions of tons of lignite/brown coal.

The work plan consisted of two phases. The objectives of Phase I were to 1) review results from work conducted at Stanford Research Institute and K-Fuel® on agglomeration methods and experiments, 2) review and recommend potential binderless agglomeration systems for K-Fuel®-treated coal, and 3) evaluate critical parameters of binderless agglomeration via comparison of lump fuel prepared from fresh and reheated K-Fuel®. Early vendor tests produced inconclusive results, and as a consequence, the scope of the Phase I pilot-scale agglomeration tests and the analytical characterization was increased to determine if briquettes of desired quality could be produced. Phase I activities expanded to include original Phase II test activities.

Based on a preliminary review of agglomeration systems, briquetting with a roll press and pelletizing with a roll and die were selected as the most reasonable methods for producing a densified material from the K-Fuel®. K.R. Komarek and Koppern offered equipment with the capability to process material using the roll press in the 550° to 750°F temperature range required. California Pellet Mill offered roll-and-die pelletizing equipment; however, it did not have the capability to process the material at the higher temperatures required.

Bench-scale pellet press experiments at the KFx Gillette, Wyoming, site and the EERC indicated that K-Fuel® can be reheated and pelletized without the aid of a binder. Further, the initial judgment of EERC personnel was that these pellets would probably have sufficient mechanical integrity to be shipped and handled. However, preliminary equilibrium moisture tests indicated that pelletizing did not function to reduce equilibrium moisture.

The inability to reduce equilibrium moisture was suggested to be due to surface defects on the pellets, chiefly circumferential cracks and poor densification at the ends. To further test the hypothesis that a tightly compacted, surface-sealed pellet (or briquette) would have enhanced resistance to moisture reabsorption, hot-briquetting tests were performed using a Komarek B100 roll press. Preliminary tests (23 tests) were performed by Tra-Det Inc., a small consultant firm located in West Virginia, and subsequent briquetting tests (92 tests) were performed at the EERC.

A qualitative assessment of each test parameter was made based primarily on the physical appearance of the briquette. Most samples were analyzed by physical and mechanical evaluation methods. Analytical work performed on various K-Fuel® products indicated that the reheated product had several differences from the original K-Fuel® product. These differences would have some effect on the briquetted product. Secondly, although we expect the general trends to hold, scaleup (i.e., commercial production utilizing a larger-diameter roll press) will produce differences in product quality relative to values observed for briquettes produced with the B100. Some of the problems noted on the B100, such as clamshelling and low crush strength, would be expected to improve on the larger unit. We would expect the optimum briquetting conditions on the B100 to be similar to those on the larger unit. With this as a qualification, the observed trends with the B100 briquettes were as follows:

- Differential thermal analysis (DTA) indicated differences between the starting fuels, and these differences impacted briquette quality.

- Better quality briquettes were produced at the high hopper temperatures. It was observed that as the temperature increased, more fines and volatiles were released from the feed. The product quality would be expected to improve if the fines and volatiles could be better utilized as “glue” for the briquetting process. This is an area that would deserve some attention in the design of the full-scale system.

- The impact of roll speed is questionable. Better briquettes (less clamshelling, shinier surface) were observed at the low-to-intermediate roll speeds. The roll speed had no effect on crush strength. The implication of this observation is that lower roll speeds are achievable only at lower feed rates. Therefore, the size of a commercial unit increases as roll speed decreases. The commercial unit specified for the Gillette plant was based on a low roll speed.

- Briquette quality appeared to be better at the lower hydraulic pressures (1600 psi) than the highest (2800 psi), with the best crush strength observed at 2000 and 2400 psi.

- The operation of the screw feeder supplying the feed to the briquetter rolls also appeared to have an impact on briquette quality. When the feed was “packed” into the unit by forcing material into the screw and keeping the screw full, better briquettes were produced. Packing was physically observed/monitored as increased amperage on the briquetter feeder.

- There were no conditions at which completely sealed briquettes (i.e., without clamshelling, edge splitting, or even trailing edge grooves) were made. The proposed mechanisms of reduced equilibrium moisture, a sealed briquette surface, and high briquette density were not demonstrated. Further, these mechanisms may not be mutually attainable. Results indicated that the equilibrium moistures of briquettes (between 7 and 8 wt% measured, 8 to 9 wt% estimated) are up to 1 wt% higher than the nonreheated feed material.

- Several tests were performed investigating particle-size impacts on briquette quality. The impact of size was examined two ways: using a feed with the same top size as previously tested but with fines added in, and with a smaller top size and fines added in. Using a feed with a broader size distribution (more fines) resulted in better briquettes in both cases, as evidenced by higher crush strengths. The feed with the smaller d_{50} appeared better.

- The overall trend of the equilibrium moisture results indicated four preliminary phenomena: 1) briquetting, as with pelleting, was not functioning to reduce the moisture reabsorption characteristics of the K-Fuel®; 2) the equilibrium moisture values of the reheated K-Fuel® briquettes, measured or estimated, were higher than that of the K-Fuel®; 3) the equilibrium moisture for any particular K-Fuel® was not decreased by the reheating and briquetting conditions; and 4) actual moisture adsorption was expected to be substantially lower than the equilibrium moisture.

The quality of the briquettes produced from the K-Fuel® product was most strongly influenced by temperature, feed particle size and distribution, and the starting feed. Other parameters such as roll speed, hydraulic pressure, and “packing” of the feeder impacted quality, but to a lesser extent. The crush strength of briquettes produced at the EERC using the B100 averaged 56 lb_f for low temperature (420°F average) and 105 lb_f for high temperature (554°F average), with crush strengths as high as 140 lb_f produced. Equilibrium moisture seemed to be purely a function of starting feed material and unaffected by processing conditions. The measured equilibrium moisture ranged from 6.1% to 8.2%. The specific gravity varied about a small range, 1.06 to 1.13. Significant improvements in crush strength are expected during process scaleup, but not in equilibrium moisture. If this higher-than-desired equilibrium moisture is effective in reducing the spontaneous combustion, then the hot briquetting may be a viable method of stabilizing and upgrading the K-Fuel® product.

On the basis of the results from the pilot-scale briquetting tests, K.R. Komarek recommended that one DH-500 briquetter be used for each process stream at the Gillette plant or four machines total. A preliminary design of a cooling system for the hot briquettes consists of three-stage cooling. The primary cooling would be close-coupled with the briquetter. Secondary cooling would occur on the conveyor belt, with tertiary cooling occurring on the stacker. Fogging, or cooling with humidified air, is the recommended cooling method. The capital cost for installing this system was estimated at $3 million, with operating costs of approximately $1.44/ton.

Task 56 – Preliminary Economic Evaluation of UCG at Saba Yoi, Thailand

Thailand's dynamic and sustained economic growth in recent decades translates into increasing electric power demand and energy production self-sufficiency becoming some of the nation's top priorities. Steadily increasing costs of domestic strip-mined coal resources approaching the limits of economical mining and dramatically increased costs of imported coal result in search and evaluation of both alternative resources (oil, natural gas) and advanced technologies such as underground coal gasification (UCG). At the same time, key strategic decisions in the energy industry are necessarily associated with growing environmental concerns reflecting both the heavily polluted industrial areas and, also, strict rules of investors financing environmentally clean technologies. UCG technology represents an alternative that would largely extend the life span of the mines utilizing domestic resources beyond the limits of conventional mining.

This project focuses on the feasibility of a UCG technology to provide commercial on-site power generation and a feedstock for petrochemical production at Nong Wa coalfield in the Sin Pun basin. The contract between the EERC and GMT Corporation, Ltd., was signed on October 9, 1996. The site characterization and interpretation of field data were completed in August 1997. The results of the geological characterization and resource evaluation indicated that the investigated coal field is not suitable for UCG process development. The representatives of the investor—DMR—were informed in detail about these unfavorable conditions during their visit to the EERC August 24 through September 5, 1997, and the EERC suggested not to proceed with further project activities. Because of the general interest in UCG and its potential chemical byproducts as well as for technology demonstration purposes, DMR recommended continuing with the project in its original scope. Consequently, the gasification test was conducted at the EERC, and activities pertaining to the general process development and the economic evaluation were performed as a subcontract by B.C. Technologies. It is important to note that this project did not confirm the expected resource quality and quantity as reported in previous investigations and numerous assumptions not representing the actual site conditions had to be employed in order to proceed with economic modeling and the evaluation of the chemical byproducts. The results indicate that even more favorable site conditions would not support economically viable UCG.

The primary findings supporting the conclusion that the targeted coal sequence was not suitable for UCG development are as follows:

1. The coal sequence on-site consists of thin (10–30 cm) layers of hard-to-soft lignite frequently interbedded with fossiliferous claystones and limestones. The weighted averages of representative properties of the coal sequence such as HHV (4.19–5.19 MJ/kg), fixed carbon content (12%–18%), high values of ash content (36%–41%), and density (1.90–2.19 g/cm^3) reflect the significant presence of the noted intercalations, which will adversely affect the in situ gasification of Nong Wa lignite. The cumulative thickness of coal with potential beneficial use is only about 36%–38% of the total coal sequence thickness, and its stratigraphic distribution is not favorable.

2. The frequent occurrence of sands, sandstones, and gravels in the overburden within the wider Nong Wa area provides the potential for groundwater transport to deeper zones.

Higher hydrostatic pressure in the coal-bound, water-bearing horizons than in the overburden and the underburden may allow in situ, potentially contaminated groundwater to move to surrounding environments if not controlled during and after gasification. Even though this potential is extremely limited by the low permeabilities of the ambient environments, the presence of fractures and faults, unknown at this time, could significantly increase the risks associated with contaminant transport out of the controlled system. Given these uncertainties, which are based only on limited hydrogeological information from the basin, the Nong Wa structure is not considered suitable for environmentally sound UCG process at this time.

Task 57 – Preparation and Combustion of CWF from a Lignite from Southern Thailand

In Thailand, coal is the major source for both power and nonpower usages. Over the past 10 years, the DMR in Thailand has been evaluating the ability of the country's coal reserves to meet its increasing utility and industrial energy needs. DMR discovered over 750 million tons of measured coal and subbituminous reserves. Most of the reserves are the subject of additional exploration and development plans, which include applying clean coal technologies (i.e., coal preparation and beneficiation techniques) to reduce the impact of coal use on the environment.

The EERC, which has for years been investigating the conversion of coal to energy-dense liquid fuels, was identified as a leading candidate to perform the development program. In response to the inquiry, the EERC prepared a four-task program to assess the responsiveness of the Sin Pun lignite to the temperature and pressure conditions of HWD. The treated material was to be slurried in water and combusted in the EERC's CTF. The remaining activity focused on Thai personnel training at the EERC in the area of clean coal technologies.

Approximately 400 kg of Sin Pun lignite was received at the EERC for testing. The lignite had a moisture-free sulfur content near 10 wt%, with over 95 wt% organic sulfur. HWD tests were conducted at 300° and 325°C using a bench-scale system. The coal–water fuel (CWF) produced from hot-water drying indicated a 10 wt% increase in attainable solids. Process gas and water analysis indicated that a portion of the coal's sulfur content was released during hot-water drying. In an effort to further reduce sulfur, HWD tests were conducted at higher temperatures and pressures. The results indicated that over 50% of the sulfur may be extracted from the coal prior to combustion. Sin Pun ash chemistry does not initially appear to create a problem when the coal is combusted in boiler systems; however, regular sootblowing should be performed to reduce the chance of excessive sintering. Fluid-bed combustion was identified as a good technology to utilize the high-sulfur Sin Pun coal without creating an emission problem.

Pilot-scale HWD tests were performed at 300° and 325°C. Slurry feed rates for the 300° and 325°C HWD tests were approximately 500 lb/hr. The overall solids recoveries for the two tests were approximately 93 wt%. The results indicate that hot-water drying made several improvements to the Sin Pun coal, including an equilibrium moisture reduction of 40%, sulfur reduction of 10%, and a modest increase in heating value. Comparison of energy density (slurry basis) for fuels with similar viscosity showed an increase from 4500 to 6070 Btu/lb at 300°C and 6090 Btu/lb at 325°C. Approximately 360 kg (800 lb) of CWF with a target viscosity of nominally 500 cP was prepared for combustion testing.

The fuel burned extremely well, with no feed problems noted during the course of the test. Fouling and slagging deposits each indicated a very low rate of ash deposition, with only a dusty layer formed on the cooled metal surfaces. The combustor was operated between 20% and 25% excess air, resulting in a flue gas SO_2 concentration averaging approximately 6500 ppm. This level indicates between 20% and 25% of the input sulfur content was captured by alkaline species, such as calcium, in the fly ash.

Personnel from Thailand’s DMR arrived in Grand Forks and completed interactive training by observing bench- and pilot-scale HWD demonstrations, CWF preparation and evaluation, and CWF combustion.

Task 58 – Optimizing Performance of the Heskett Station

The potential economic implications of switching bed material from sand to limestone at the MDU R.M. Heskett Station were determined. Plant data were obtained for the last 4 years of operation. The average of 1996, 1997, and 1998 was used. Data from 1995 were not considered because of a low capacity factor for that year. The switch from the sand bed to limestone impacts the overall plant economics in three primary ways. First is the direct savings due to the lower cost and lower usage rate of the limestone. If limestone were to replace sand at the current feed rate, an annual savings of $35,000 would be realized. If limestone were to replace the sand at the lower feed rate of 2.5% of the coal feed rate compared to 5.41% for the sand, the savings would be more substantial. $200,000 annual savings are possible as a result of the lower usage rate and lower cost of the limestone.

A second factor to be considered is the value of the SO_2 allowances that will be generated by the use of limestone. Over the past year, the price of allowances has risen from under $100 to near $200/ton SO_2. At an allowance price of $200/ton SO_2, gross annual revenues ranging from $390,000 to $650,000 ($275,000 to $455,000 net [gross revenues minus limestone cost]) could be realized. Since the cost of the limestone required to generate 1 ton of SO_2 credit is $60, and provided MDU can market the credits generated from the plant, the most economical approach is to add limestone at a much higher feed rate than is necessary to avoid agglomeration. As mentioned previously, however, the effectiveness of additional limestone feed to capture sulfur diminishes after a limestone:coal ratio of about 5; care must be taken to optimize SO_2 emissions without increasing limestone feed past the point of minimal return.

The third factor that affects bottom-line economics is the overall plant efficiency. One of the goals of the test burn was to reduce operating costs by determining the optimum excess oxygen for the boiler. Significant cost savings can be realized by avoiding the high unburned carbon losses when operating below 3% excess oxygen. For low-load operation, reducing the excess oxygen by 1.5% would reduce the annual operating cost by $64,000 times the fraction of the time the unit is operated at low load, or approximately $25,000 to $30,000 per year. The costs associated with efficiency loss were based only on the potential fuel savings.

Finally, overall unit availability can be improved with a switch from sand to limestone bed material. The test burn clearly showed that the potential for agglomeration is greatly reduced with the addition of limestone; reducing the number of forced outages caused by bed agglomeration will significantly improve availability.

The overall conclusion from this work is that a switch from river sand bed material to limestone at the R.M. Heskett Station would provide substantial benefits to MDU. A switch to limestone would increase the fuel flexibility of the unit, allowing fuels higher in both sodium and sulfur to be burned. The limestone bed can tolerate a much higher buildup of sodium in the bed without agglomeration, allowing either the bed turnover rate to be reduced to half the current sand feed rate for a fuel with equivalent sodium or allowing a higher-sodium fuel to be burned with limestone feed rates equivalent to the current sand feed rate. Both stack and ambient SO_2 emissions can be controlled. A small improvement in boiler efficiency should be achievable by operating at lower excess oxygen levels at low load. This reduction in oxygen will also lower NO_x emissions, providing a margin of safety for meeting emission standards. No detrimental effects of using limestone at the Heskett Station were uncovered as a result of the test burn. Some specific conclusions from this work include the following:

- The bed material feed rate can be reduced from the current rate of 5.4% of the coal feed rate (57.4 tons of sand/day) to 2.5% of the coal feed rate (27 tons of limestone/day). This will result in an annual savings of approximately $200,000.

- SO_2 emissions at the recommended feed rate would be approximately 250 ppm (0.82 lb/MMBtu) using a similar lignite. Based on the cost of the limestones, SO_2 allowances could be generated at a cost of $60/ton SO_2, leaving a large profit margin for the sale of allowances. The addition of limestone at the same rate currently used for sand feed could generate $455,000 net income if allowances are sold at $200/ton SO_2.

- At full-load operation, unburned carbon losses increase significantly at excess oxygen levels below 2.8%. No efficiency gains are expected at high-load operation by switching from sand to limestone. Reducing the oxygen level at low load to 8.5% would allow an efficiency gain of approximately 1.2% to be realized, equating to $25,000 to $30,000 in annual savings.

- A reduction of 25 tons/day total ash (bed material plus fly ash) will be realized by using limestone at the recommended feed rate compared to the current sand feed rate. No measurable change in volume would be realized because of the lower bulk density of the limestone-derived material.

Task 59 – Binder Modification and Development for Briquetting Steel Mill Residues

Alternatives to the molasses–ordinary portland cement (OPC) binder for steel mill residues were extensively investigated. A large number of binder modifications were tested using a hand-pelleting apparatus to identify effective compositions. The more effective compositions were evaluated using the Komarek press. Evaluations consisted of drop tests, compression tests of green and cured pellets, and tumble tests of cured pellets. Pyrolysis odor tests were performed to determine the effects of certain compositions on the disagreeable “wet campfire” odor produced during heating of the molasses–OPC briquettes. Scanning electron microscope morphology studies were conducted to examine the structures formed during briquetting.

Several tacky polymers were investigated as alternatives to the molasses compositions. A water-soluble form of polyvinyl alcohol (PVA) gave high-strength pellets and briquettes at low concentrations of binder (1%). Pyrolysis odor tests showed that the PVA pellets generate the wet campfire odor. Clay binders were investigated using montmorillonite and bentonite clays in various compositions, excluding molasses. Both green and cured strengths were relatively poor. A clay–PVA binder composition gave a much stronger pellet. Cost of the PVA would be high; thus, further work with alternative organic binders was not pursued.

Binders were prepared from two types of fly ashes. Several other inorganic binders were investigated in combination with lime and OPC. Briquetting tests with the Komarek press showed that the fly ash, hydrated lime, and sodium silicate binder systems are ineffective at providing tumble resistance that approaches that of the baseline (OPC, molasses, water). Further, without the aid of a significant level of moisture, none of these binder systems provide the necessary green drop–shatter resistance that the molasses imparts.

The addition of salts of trivalent ions such as aluminum and iron to the molasses results in a dramatic decrease in the viscosity of the molasses. Consequently, the binder is able to coat or wet the steel waste much more effectively and much stronger binding occurs. Pellets produced using aluminum or ferric nitrate were about 30% stronger. Less molasses–salt binder can be used to produce the same strength as molasses alone. Other salts, such as sulfates and chlorides, were also effective in increasing the binder strength of the molasses.

Pyrolysis odor tests demonstrated that eliminating the calcium from the binder changes the wet campfire odor to one more like burned sugar and burned wood. Further addition of nitrate salts reduces the odor significantly at lower temperatures, presumably by oxidizing the odor-producing constituents.

The modified molasses–salt binders represent a significant advance in binder technology in increasing the strength and abrasion resistance of briquettes. The potential for odor control needs further investigation. Additional benefits that can be obtained from these binder systems are 1) reduction in slag owing to elimination of inerts such as portland cement or hydrated lime, 2) reduction in furnace fuel requirements owing to lower heat burden for melting inert binder components, 3) simplification of the briquetting process, and 4) reduction of material handling. The cost of the additives has not been evaluated, but utilizing a small unit to convert steel waste to iron nitrate or sulfate might be considered.

Task 60 – Characterizing Soil/Water Sorption and Desorption Behavior of BTEX and PAHs Using Selective Supercritical Fluid Extraction (SFE)

The first goal of the proposed study was to generate initial data to determine the ability of selective SFE behavior to mimic the soil/water sorption and desorption behavior of BTEX and PAHs. Samples generated by Professor Bill Rixey's column sorption studies (aged for 2 weeks to 8 months) and desorption studies (6 weeks' desorption of the aged soil columns with pure water) were extracted using sequentially stronger SFE conditions to selectively remove different fractions of each BTEX and PAH component, which range from "loosely" to "tightly" bound in the soil matrices. The selective SFE results parallel the sorption/desorption leaching behavior and mechanisms determined by Professor Rixey's investigations (under separate funding) using water desorption of soil columns previously aged with BTEX and PAHs. These results justify more intensive investigations of the use of selective SFE to mimic soil/water sorption and desorption of organic pollutants related to fossil fuels, which will be performed under separate funding.

The second goal of the study was to determine if selective SFE extraction behavior parallels the remediation behavior displayed by PAHs currently undergoing in-situ bioremediation at a manufactured gas plant (MGP) site. On the basis of soil analyses of several individual PAHs (as well as total PAHs) before remediation began and after 147 days of remediation, selective SFE can be said to successfully mimic remediation behavior. These results strongly support the use of selective SFE to predict remediation behavior of soils contaminated with PAHs and are expected to provide a powerful and rapid analytical tool that will be useful for determining the remediation endpoints necessary for environmental protection. Based on the initial success found in the present study, additional investigations into the use of SFE for predicting and monitoring the remediation behavior of PAH-contaminated soils will be performed under separate funding.

Task 61 – Characterization of a Fluidized-Bed Combustion Ash to Determine Potential for Environmental Impact

Because of the low concentrations of potentially problematic trace elements found in these ash leachate samples, it is highly unlikely that this ash could present any adverse risk or threat to the environment. Concentrations in leachate were for the most part low enough that interpretation concerning long-term leaching (LTL) trends were difficult to make. Most LTL results were in a low enough range that expected experimental error was greater than some of the measurements, many of which were just above lower limits of quantitation (LLQs). The following can be stated:

- In spite of a relatively high moisture content, the fuel fed very well, maintaining a very uniform temperature distribution throughout the reactor. While the calcium-to-sulfur ratio was higher than expected for Test 1, optimization of the operating temperature could decrease limestone requirements.

- The NO_x emissions generated during the combustion tests are higher than would be generated at full scale. Wall effects are the absence of secondary air in the bench-scale reactor resulting in higher NO_x; testing at a larger scale may be necessary to accurately predict full-scale NO_x.

- The results of the selective noncatalytic reduction (SNCR) test suggest that this method of NO_x reduction may be inappropriate for this fuel under CFB conditions. The higher temperatures required for effective NO_x reduction have a dramatic negative impact on sulfur retention, so that optimizing one parameter will seriously compromise the other. Because of the strong effect of temperature on sulfur capture for this fuel, operating at a "middle ground" condition may result in excessive levels of both NO_x and SO_2. SNCR could be effective if some type of reburn were used to raise flue gas temperatures prior to SNCR, while maintaining the furnace at a lower temperature to optimize sulfur capture. Other methods of NO_x reduction, including air staging and optimization of Ca:S and excess air, may provide acceptable emission levels.

- RCRA standards were not exceeded in any of the leachates. Concentrations of RCRA constituents were nearly all below drinking water standards.

- Leachate solution concentrations of major and minor constituents are very low, except for calcium and sulfate. Since calcium and sulfate are present in relatively high concentrations, with sulfate concentrated on the surface of spent bed material as well as ash particles, it would be expected that the solubility of calcium sulfate, which is relatively high, would be a major factor in determining the chemical composition of the leachate.

- While ettringite was a primary hydration product in all of the leached materials, the low concentrations of oxyanionic trace elements, along with the lack of significant documentable trends in leachate concentration evolution, made it difficult to determine exactly what role ettringite formation played in trace element leaching. It is known that ettringite formation can result in what is referred to as anomalous leaching, resulting in a decrease in leachate concentration of select trace elements with respect to time. For this to be documented, however, it is necessary to have significant concentrations of the trace elements, which were simply not present in these samples.

- Overall, the large number of extremely low or less-than values further attest to the benign nature of these as well as most other CCBs.

Interaction of leachates with the local geologic material was an aspect of environmental impact that was not a part of this project, but must be considered in the interpretation of these data. After leachate migrates from a disposal site, varying factors will continue to influence the concentrations of leached materials. Under normal geological and hydrogeological conditions, dispersion, diffusion, and dilution with groundwater will all lead to lower constituent concentrations. Additionally, many geologic materials have attenuating properties that can further reduce the concentrations of trace constituents. Cation and anion exchange as well as precipitation and sorption effects will likely even further reduce constituent concentrations in leachate.

Task 62 – Reducing Power Production Costs by Utilizing Petroleum Coke – Annual Progress Report

The first year of a 2-year investigation of the effects of blending petroleum coke with PRB subbituminous coals on grindability, electrostatic precipitator (ESP) particulate collection efficiency, combustion reactivity, and fouling/slagging was completed. Preliminary observations and conclusions include the following:

- Samples of a PRB coal, petroleum shot coke, and coal–coke blends of 95/5 and 85/15 (on a weight basis) were pulverized under identical conditions. Summations of the Ni and V contents for three size fractions (<45 µm, ≥45 µm but <75 µm, and ≥75 µm) of the fuels indicate that the finest particle-size fraction of the petroleum coke is significantly enriched in V and Ni relative to its coarser size fractions. In contrast, V and Ni are uniformly distributed among the three particle-size fractions of the pulverized PRB coal. The finest particle-size fractions of the coal–coke blends are not enriched in V and Ni relative to their coarser size fractions, suggesting that the softer Ni- and V-depleted coal particles are preferentially fractioned into the finest size fractions during pulverization.
- Combustion testing of the PRB coal and two coal–coke blends in a 40,000 Btu/hr downfired combustion system indicates that the primary effect of petroleum coke blending on flue gas composition is a significant increase in sulfur concentration. Sulfur speciation analyses indicate that although SO_2(g) concentrations increase significantly with increasing coke blending, SO_3(g) remains undetectable. Mass balance calculations suggest that increasing coke blending promotes the conversion of fuel sulfur to inorganic SO_4 compounds in the fly ash. Chemical analyses of fly ashes collected in the baghouse confirm the direct relationship between coke blending and sulfation of the fly ash. In addition to sulfur, the V concentrations of the ashes increase significantly with increasing coke blending, suggesting that V^{+5} catalysis of SO_2(g) oxidation is responsible for the increase in fly ash sulfation. An x-ray absorption fine-structure spectroscopy analysis confirmed the presence of V^{+5} in the 85/15 blend ash.
- Deposit samples from PRB coal–petroleum shot coke blends (coke blends of 0, 10, and 20 wt%) were produced in a drop-tube furnace under slagging and high-temperature fouling conditions.
- The morphological (e.g., porosity, degree of crystallization, ash particle size and sphericity) and chemical characteristics of the deposits were determined using x-ray diffraction, SEM, electron probe microanalysis, and digital image analysis techniques.
- Measurements of deposits, produced from burning PRB coal–petroleum shot coke blends (coke blends of 0%, 10%, and 20% on a weight basis) in a drop-tube furnace under slagging and high-temperature fouling conditions indicate that petroleum coke blending with PRB coal impedes the rate of fouling deposit growth but promotes slag deposit strength.

Year 2 Work Plan

Work during the second and final year of this project will continue as Task 8 under the follow-on Cooperative Agreement DE-FC-26-98-FT40321. Year 2 will primarily involve the following activities:

- Chemical and morphological analyses of fouling and slagging deposits
- Continuation of fouling and slagging assessments, including the determination of initial slagging temperatures for three blends using the ODTF
- Fuel reactivity and combustion efficiency testing using the ODTF
- Evaluation of ash utilization properties
- Preparation of an annual and a final report
- Presentation of research results at an appropriate conference.

Task 63 – Characterization and Modeling of the Forms of Mercury from Coal-fired Utility Power Plants

The 1990 CAAAs required EPA to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* and *Utility Air Toxics Report to Congress*. The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam–electric generating units. Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations would be required. However, they did indicate that the EPA views mercury as a potential threat to human health. The EPA indicated that additional research/information was necessary before any definitive statement could be made. This has led the EPA to issue an Information Collection Request (ICR).

In addition to understanding mercury behavior in the environment, the chemical form of the mercury emissions also appears to determine the effectiveness of controls to remove mercury because of the markedly different chemical and physical properties of the different mercury forms. For example, on the basis of chemical principles, Hg^0 should not be absorbed significantly by water-based scrubbing processes because it has a very low water solubility. On the other hand, the high water solubility of $HgCl_2$ suggests this species should be effectively removed by wet scrubbing. The effectiveness of mercury control by activated carbon or other solid sorbents is also dependent on the mercury species present. Research to date suggests that flue gas mercury removal efficiencies are strongly dependent on the mercury species present.

Mercury sampling had been completed at a number of facilities; however, in several cases only total mercury was measured and for those where mercury speciation measurements were attempted, substantial questions arise as to the validity of the data. The two methods commonly used to speciate mercury were EPA Method 29 and the MESA method. Research at the EERC, Radian, and other laboratories have shown that under certain conditions both of these methods do not adequately speciate mercury.

Because of unique capabilities of both the EERC and Radian, International, a teaming arrangement was put in place and was funded by DOE and EPRI. The work at the EERC was funded under the JSRP program, while the Radian work was funded exclusively by EPRI. The primary focus of the work was to measure the different mercury species (Hg^0 and Hg^{2+}) at several utilities. The data were then used to help model the mercury forms in the flue gas based on relatively simple inputs such as coal type, coal analysis, and plant configuration. This is an ongoing project and is not scheduled to be completed until August 1999.

Project Objectives

The primary objective of the project was to develop models that would be able to predict mercury speciation in flue gas from coal-fired systems on the basis of such variables as coal type, coal analysis, and plant configuration. Specific objectives of the project were as follows:

- To characterize the form of mercury emissions from different power plants.

- To complete a series of bench-scale studies to help determine the mechanisms of mercury speciation and fly ash–mercury interactions.

- To validate the Ontario Hydro mercury speciation method in the field.

Project Status

To complete the project, the EERC and Radian were each given specific responsibilities. Radian was to do the actual field sampling and data correlations as well as some of the bench-scale work. The EERC was responsible for the analyses of the field samples, data reduction, and the report on validation of the Ontario Hydro method and also for some of the bench-scale work. The reports were to be jointly written.

To date, two power plants have been sampled for mercury. The first was a western plant, referred to as Site 111, that burned a western bituminous coal. This plant had two units, both with a baghouse. In addition to the baghouse, Unit 2 also had a FGD system. The results from the sampling activities from this plant showed that the fly ash was highly reactive toward mercury. At the inlet to the ESP, over 90% of the mercury was measured as particulate-bound mercury when the sample filter was maintained at 250°F. The small amount of mercury that was measured in the gas phase was almost all Hg^{2+}.

The second plant was an Ohio power plant that burned an Ohio bituminous coal. This plant had an ESP for particulate control and a wet FGD system to control SO_2 emissions. The field validation of the Ontario Hydro mercury speciation method was done at this plant. This plant was chosen because the high sulfur and chloride content of the coal would provide a challenge to the method. In addition, pilot-scale tests done with this coal indicated that the concentration of elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) was well above the comfort level of detection for the method (>0.5 µg/Nm^3). The field validation work was done using quadtrains at a sample port located at inlet to the FGD unit (outlet of the ESP). The results clearly show that the Ontario Hydro method meets the criteria for precision and bias as stated in EPA Method 301.

After completion of the mercury sampling at the two plants, the sampling activities were put on hold when EPA issued the ICR. Because the ICR was going to require a substantial number of power plants (70–80) to measure speciated mercury, it was not necessary to measure mercury independently of the ICR. The sampling activities may resume once EPA has decided what plants will be required to sample for mercury.

Radian has begun some of the bench-scale work. It has evaluated the adsorption capabilities and reactivity of over a dozen different fly ashes. A report has not yet been issued on this work. The bench-scale work at the EERC will be begin after January 1, 1999. Also some very preliminary correlations for the modeling activities have been completed by Radian, but there have not been any models developed, as more data are needed.

Task 64 – Mercury Formation and Fate

Mercury is emitted by both natural and human processes, and cycles through atmospheric, aquatic, and terrestrial environments. Forms of mercury that appear most important in these environments are elemental mercury (Hg^0), inorganic or oxidized mercury (Hg^{2+}), and monomethylmercury. The chemical form of mercury affects its transport through air, land, and water, as well as chemical and biological behavior. Hg^0 is known to circulate in the atmosphere for about 1 year before it is deposited. Hg^{2+} in the atmosphere can be deposited directly to water bodies or can be transported from land by runoff and enter ponds, streams, rivers, lakes, etc. The water bodies contain microorganisms that have the metabolic capability to carry out chemical reactions that bind oxidized mercury to methyl groups, producing methylmercury. Humans and wildlife are generally exposed to methylmercury, usually from eating fish that have accumulated methylmercury in their muscle tissue. Methylmercury can produce a variety of adverse health effects, depending on dose and time of exposure.

Determining mercury contributions to lake environments from anthropogenic sources such as power plants requires an understanding of natural background levels of mercury within the watershed geology and preindustrial sediments. Several studies have shown that significant variation of mercury concentrations exists within varying bedrock materials. Many studies have shown increasing mercury concentrations in more recently deposited (postindustrial) lake bottom sediments. This has been used as evidence for increased atmospheric input. However, other factors such as geochemical and geomechanical processes may also be responsible for these increasing trends.

To determine the speciation and levels of mercury emissions from North Dakota Power plants and if these emissions impact the Devils Lake area, a consortium was set up. A contract was put in place with the EERC to measure mercury emissions from two North Dakota power plants and to determine the level of mercury in sediments in Devils Lake. The consortium consisted of the following groups.

- Minnkota Power Cooperative, Inc., the owner and operator of the Milton R. Young Station, located near Center, North Dakota
- Cooperative Power Association, the owner and operator of the Coal Creek Station located near Underwood, North Dakota
- North Dakota Industrial Commission
- DOE –EERC JSRP
- EPRI

Project Objectives

The overall objective of the project was to provide information that would assist in determining the potential impact of mercury emissions from North Dakota lignite-fired power plants on the bioavailability of mercury to humans.

To help accomplish this, the project was divided into two tasks. (Complete project reports for both Tasks 1 and 2 are available). Task 1 focused on determining the abundance and forms of mercury emitted from two North Dakota power plants. Task 2 was to address discrepancies noted in the literature regarding the source of mercury in lakes and determine mercury concentrations in lake bottom sediments and glacial till deposits within the watershed area.

The three primary objectives of the Task 1 sampling effort at the two North Dakota power plants were as follows:

- Determine the speciated mercury emissions from each of the two coal-fired electric utilities.
- Provide ESP and FGD removal efficiencies for each the mercury species.
- Determine the mercury material balances at each of the plants.

For Task 2, characterization of lake bottom sediments from Devils Lake, the primary objective was to determine the potential contributions that geological setting and geological processes other than atmospheric deposition may have on mercury concentrations in lake sediments. A secondary objective of the activities was to provide updated information regarding the nature and extent of mercury in Devils Lake and its watershed.

Approach

Task 1. The general approach to the sampling activities at both power plants was to determine the mercury speciation before and after the wet FGD system and ESPs, and to determine the speciated mercury emissions at the stack. All mercury speciation measurements were made using the Ontario Hydro method, which has been validated in pilot- and field-scale tests by the EERC.[3] The mercury balances were then obtained by collecting and analyzing the solid samples (coal, ESP hopper ash, and FGD sludge) and the liquid samples (FGD makeup water, FGD blowdown, settling pond, lime/fly ash slurry water). In this way, a determination was made as to the concentration and species of mercury being emitted to the atmosphere as well as the fate of mercury generated during the combustion of North Dakota lignite.

Task 2. The characterization of lake bottom sediments was carried out from two locations in Devils Lake—Creel Bay and Six-Mile Bay. Although the selection of the specific sampling sites was based on an evaluation of information from a variety of sources, these two locations represented a majority of the drainage basin lithology in which Devils Lake is set. The glacial till samples were taken from three separate areas approximately 4 miles west, 3 miles northwest, and 3 miles northeast of the city of Devils Lake. The bulk sediments collected were analyzed for mercury, other trace metals, and organic content. In addition, the <63-µm fractions from the cores were analyzed separately. ^{210}Pb modeling and pollen analysis were conducted to support chronological assessment of sediment accumulation rates and elemental distribution in lake bottom sediment profiles.

Project Results and Conclusions

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[3] Laudal, D.L.; Heidt, M.K. *Evaluation of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-108988; Dec. 1997.

There were some minor differences between the two coal-fired power plants as to the fate of the generated mercury. However, the mercury results showed the two power plants were much more similar than different. At both plants, the mercury measured prior to the ESP was primarily in the form of Hg^0 (>85%). The small amount of Hg^{2+} that was generated was removed effectively by the FGD systems. For both plants, little of the mercury was removed by the ESPs. At the Milton R. Young Station, the ESP removed about 5% and at Coal Creek essentially zero. The mercury emissions at the stack for both plants are shown in the table below. It should be noted that the small amount of Hg^{2+} measured at the stack is a result of a portion of the flue gas bypassing the FGD system for reheat purposes.

Emission Factors for Mercury

Plant	**Hg^{2+}, lb/10^{12} Btu**	**Hg^0, lb/10^{12} Btu**	**Total Hg, lb/10^{12} Btu**
Coal Creek	0.83 ± 0.14	7.78 ± 0.94	8.70 ± 1.01
Milton R. Young	0.89 ± 0.15	7.85 ± 0.69	8.74 ± 0.81

The mercury captured by the FGD systems was almost entirely associated with the solid portion of the FGD sludge and appeared to be very stable. Also, the calculated mercury balances for both plants were excellent (±10%).

As stated earlier, Hg^0 is known to circulate in the atmosphere for over a year before deposition, while Hg^{2+} is generally deposited either locally regionally. Therefore it is unlikely that either of these coal-fired electric utilities was directly responsible for the mercury levels in Devils Lake. Their responsibility lies only in that they are adding to the global mercury burden. This appears to be supported by the Task 2 work, characterization of Devils Lake sediments.

In the Task 2 activities, the mercury concentrations in sediments for Six-Mile Bay ranged from 30 to 66 ng/g and from 42 to 140 ng/g in Creel Bay cores. Both mercury and other trace metals were found to have similarly increasing concentration trends and correlated positively with increasing proportions of finer fractions of the lake sediments. Similar trends were found with organic content.

It has been suggested by some researchers that the distribution of mercury accumulation rates is strongly positively correlated with the ratio of watershed-to-lake surface area. However, relatively steady increases in mercury concentration in the Six-Mile Bay sediment profile and corresponding extremes associated with minimal lake levels in 1940 and 1965 do not provide evidence to support this hypothesis.

The core samples indicated that mercury concentration has increased since about 1880; however, there are corresponding increases in other trace elements as well. The only significant trace element emitted from the two power plants is mercury. The other trace elements are collected by the highly efficient ESPs. If these plants were directly responsible for mercury deposition in Devils Lake, it would be expected that in the past 20 years there would have been a corresponding increase in mercury above the increase in other trace elements. This is clearly not the case.

On the basis of the current data, it can be concluded that watershed characteristics, water level fluctuation, and anthropogenic impact result in significantly larger mercury and trace metal enrichment than potential contribution from atmospheric sources.