

JV TASK 6 – COAL ASH RESOURCES RESEARCH CONSORTIUM RESEARCH

Final Report

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ABSTRACT

The Coal Ash Resources Research Consortium® (CARRC®, pronounced “cars”) focuses on performing fundamental and applied scientific and engineering research emphasizing the environmentally safe, economical use of coal combustion by-products (CCBs). 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 U.S. Department of Energy is a partner in CARRC through the EERC Jointly Sponsored Research Program (JSRP), which provides matching funds for industrial member contributions and facilitates an increased level of effort in CARRC.

CARRC tasks were 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 special projects are developed with members and nonmembers to provide similar information and to support activities, including the assembly and interpretation of data, support for standards development and technology transfer, and facilitating product development and testing.

CARRC activities from 1998 to 2007 included a range of research tasks, with primary work performed in laboratory tasks developed to answer specific questions or evaluate important fundamental properties of CCBs. CARRC topical reports were prepared on several completed tasks. Specific CARRC 1998–2007 accomplishments included:

- Development of several ASTM International Standard Guides for CCB utilization applications.
- Organization and presentation of training courses for CCB professionals and teachers.
- Development of online resources including the Coal Ash Resource Center, Ash from Biomass in Coal (ABC) of cocombustion ash characteristics, and the Buyer’s Guide to Coal-Ash Containing Products.

In addition, development of expanded information on the environmental performance of CCBs in utilization settings included the following:

- Development of information on physical properties and engineering performance for concrete, soil–ash blends, and other products.
- Training of students through participation in CARRC research projects.
- Participation in a variety of local, national, and international technical meetings, symposia, and conferences by presenting and publishing CCB-related papers.

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EXECUTIVE SUMMARY

The Coal Ash Resources Research Consortium® (CARRC®, pronounced “cars”) is the core coal combustion by-product (CCB) research group at the Energy & Environmental Research Center (EERC). CARRC focuses on performing fundamental and applied scientific and engineering research emphasizing the environmentally safe, economical use of CCBs. 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 U.S. Department of Energy is a partner in CARRC through the EERC Jointly Sponsored Research Program (JSRP), which provides matching funds for industrial member contributions and facilitates an increased level of effort in CARRC.

CARRC tasks were 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 special projects are developed with members and nonmembers to provide similar information and to support activities, including the assembly and interpretation of data, support for standards development and technology transfer, and facilitating product development and testing.

CARRC activities from 1998 to 2007 included a range 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 this report are 1) Standards Development, 2) Determination of the Rate of Hydration and Reaction Products, 3) Assembly of NORM Data on CCBs, 4) Mercury Issues Related to CCB Utilization, 5) Evaluation of Fly Ash and Fly Ash Sorbent Blends for Mercury Release and Utilization Potential, 6) the Use of CCBs in the Management of Feedlot Wastes, 7) Technical Evaluation of Rammed-Earth Products, 8) CCBs from Combustion of Coal with Other Fuels, 9) Buyer’s Guide to Coal-Ash Containing Products, 10) Development of Beneficial Use Policy for Bottom Ash, 11) Evaluation of Coal Fly Ash Variability, 12) Comparison of Available Swell/Expansion Tests and Development of an Expansion Test for CCBs, 13) Handling and Use of Wet and Dry FGD Material, 14) Utilization of Sulfite-Rich FGD Material, 15) Review of Literature on Spray Dryer Absorber Material, 16) Environmental Performance of CCBs, 17) Evaluation of Current Leaching Procedures, 18) Characterization of Ammoniated Ash, 19) FlexCrete Feasibility Study, 20) Sediment Attenuation Effects on Coal Ash Leachates, 21) Freeze–Thaw Study, and 22) Education and Training.

CARRC topical reports were prepared on several completed tasks:

- The Impact of Ammonia on the Leaching of Selected Constituents from Coal Fly Ash
- Review of Handling and Use of Wet and Dry FGD Materials

- Use of Fly Ash and Bottom Ash in Rammed-Earth Construction
- Comparison of Dry Scrubber and Class C Fly Ash in Controlled Low-Strength Materials (CLSM) Applications
- Evaluation of Variability of Coal Fly Ash from Midwestern Utilities
- Feedlot Stabilization Using Coal Combustion By-Products: An Annotated Bibliography
- Buyer's Guide to Coal Ash-Containing Products
- Turtle Mountain Band of Chippewa Flexcrete™ Production Market Feasibility Study
- Naturally Occurring Radioactive Materials in Coal Combustion By-Products

CARRC 1998–2007 accomplishments included:

- Development of several ASTM International Standard Guides for CCB utilization applications.
- Organization and presentation of training courses for CCB professionals and teachers.
- Development of online resources including the Coal Ash Resource Center, Ash from Biomass in Coal (ABC) of cocombustion ash characteristics, and the Buyer's Guide to Coal-Ash Containing Products.

Development of expanded information on the environmental performance of CCBs in utilization settings:

- Development of information on physical properties and engineering performance for concrete, soil-ash blends, and other products.
- Training of students through participation in CARRC research projects.
- Participation in a variety of local, national, and international technical meetings, symposia, and conferences by presenting and publishing CCB-related papers.

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1.0 INTRODUCTION

The Coal Ash Resources Research Consortium (CARRC) has worked to advance coal combustion by-product (CCB) management and utilization since 1985 and is a key research program at the University of North Dakota (UND) Energy & Environmental Research Center (EERC). The CARRC research approach has always focused on performing research and technology transfer activities that address industry needs as defined by CARRC members. CARRC leverages industrial research dollars by matching them with funds from the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL) through the EERC's Jointly Sponsored Research Program (JSRP). CARRC also provides an information and discussion conduit between industry and DOE NETL. For the past 21 years, CARRC partnerships have focused on the overriding CARRC goal of promoting the environmentally safe, technically sound, and economically viable management of CCBs.

CARRC provides a forum for members to discuss and identify technical issues that are currently impacting, and/or are expected to impact, the management of CCBs. To address these issues, CARRC members and researchers work together to develop CARRC tasks. The tasks can be categorized as follows:

- Member-prioritized research tasks
- Technology transfer and maintenance tasks
- Special projects

All tasks are designed to work toward achieving the CARRC overall goal and supporting objectives. The various tasks are coordinated in order to provide broad and useful technical data for CARRC members. Special projects provide an opportunity for non-CARRC members to sponsor specific research or technology transfer consistent with CARRC goals.

This report covers CARRC activities from 1998 through 2007. These activities have been reported in CARRC Annual Reports and in member meetings over the past 9 years. CARRC continues to grow and work with industry and various government agencies with its 22nd year of research, development, demonstration, and promotional activities nearing completion at the time of submission of this report. CARRC expects to continue its service to the coal ash industry in 2008 and beyond to work toward the common goal of advancing coal ash utilization by solving CCB-related technical issues and promoting the environmentally safe, technically sound, and economically viable management of these complex and changing materials.

1.1 CARRC Industrial Members

Those who have been CARRC members during the 1998–2007 period are gratefully acknowledged for their participation and cooperation in CARRC activities:

- Alliant Energy
- Ameren
- Ash Resources
- Boral Materials Technologies
- Great River Energy
- Headwaters Resources
- Indianapolis Power & Light Company
- Ish, Inc.
- Lafarge North America
- Otter Tail Power Company
- Tennessee Valley Authority
- U.S. Department of Energy National Energy Technology Laboratory
- Xcel Energy

The following industrial groups and government agencies have also provided funding for CARRC special projects from 1998 through 2007:

- American Coal Ash Association, Inc.
- Basin Electric Power Cooperative
- Boral Material Technologies, Inc.
- Building Products & Concrete Supply, Ltd.
- Charah
- Environmental Resource Corporation
- Electric Power Research Institute (EPRI)
- Great River Energy
- Headwaters
- International Polymer Corporation
- International Pozzolan Coating Company
- Ish, Inc.
- Lafarge North America
- Lehigh Cement Company
- Minnkota Power Cooperative
- North Dakota Industrial Commission
- Otter Tail Power Company
- Pacificorp
- Pozzi-Tech, Inc.
- Salt River Materials Group
- Santee Cooper
- Separation Technologies, LLC
- State Board of Agricultural Research & Education
- Synthetic Materials (SYNMAT)
- Temple Inland
- Tennessee Valley Authority
- Turtle Mountain Band of Chippewa
- Utility Solid Waste Activities Group

- Western Region Ash Group
- Xcel Energy

CARRC also acknowledges Mr. Robert Patton, the DOE NETL Project Manager for CARRC. In 2005–2007, CARRC implemented an advisory board of up to three industry professionals who serve to provide input to the overall CARRC program and individual activities. Those advisors include Mr. David Goss, Executive Director, American Coal Ash Association; Mr. Ken Ladwig, Program Manager, EPRI; and Mr. Michael Thomas, formerly Wenck Associates. Their assistance has been valuable in continuing the CARRC Program, and CARRC researchers and members wish to acknowledge their participation.

1.2 CARRC Research Staff

The EERC's multidisciplinary approach to research is well demonstrated in CARRC research and related activities. CARRC has the opportunity to draw from the diverse research staff at the EERC while maintaining a core staff that focuses on CCB utilization and disposal research. Key to this approach is communication among numerous individuals and groups as well as the coordination of sample identification, collection, distribution, and data manipulation. The core EERC CARRC research group consists of the following individuals:

Debra F. Pflughoef-Hassett, CARRC Program Manager
 Tera D. Buckley, Market Research Specialist
 Bruce A. Dockter, Research Engineer
 Kurt E. Eylands, Research Geologist
 David J. Hassett, Research Chemist
 Loreal V. Heebink, Research Chemist
 Erick J. Zacher, Research Geologist

CARRC researchers continue to work with Oscar E. Manz, Professor Emeritus, Civil Engineering, UND, who was instrumental in developing CARRC and continues to have strong ties to the CCB industry nationally and internationally.

CARRC also employs and trains graduate and undergraduate students at UND both through direct participation in CARRC activities and through parallel efforts in various academic departments. Students were directed by CARRC researchers and provided valuable information and skills that enhanced CARRC activities. A primary advantage of the work performed by these students is the knowledge and experience they take with them as they move into technical and professional careers. CARRC researchers wish to acknowledge the following students for their role in advancing CARRC research during 1998–2007:

Erika Bartley, Larimore High School
 Amber Bruns, Forensic Science, UND
 Tera Buckley, Marketing, UND
 Dean Comber, Computer Science, UND
 Robert Ducioame, Physics, UND

Amy Gieske, Mechanical Engineering, UND
Monique Goeden, Clinical Laboratory Science, UND
Loreal Heebink, Chemistry, UND
Heather Holden, Undergraduate, UND
Jeff Hovde, Chemistry and Secondary Education, UND
Dustin Kouba, Red River High School
Josh Mason, Information Technologies, UND
Linnea Schluessler, Mechanical Engineering, UND
Sarah Thomasson, Chemistry and Pre-Medicine, UND
Candace Weager, Undergraduate, UND
Kendra Wubbema, International Studies, UND
Erick Zacher, Environmental Geology and Technology, UND

2.0 BACKGROUND

Since its inception in 1985, CARRC (called the Western Fly Ash Research Development and Data Center [WFARDDC] until 1993) has evolved in its goals and its activities as well as steadily increasing its membership. From 1985 to 1993, CARRC (WFARDDC) was funded solely by industrial sponsors and focused on the utilization of western fly ash primarily in cementitious applications with the primary goal to develop the best means of characterizing those materials to ensure their technically sound use in concrete, concrete products, and other cementitious applications. Those activities were reported in “A Database of Chemical, Mineralogical, and Physical Properties of Coal Fly Ash—A Research, Utilization, and Disposal Aid” (Pflughoef-Hassett, D.F.; Hassett, D.J.; McCarthy, G.J.; Manz, O.E.; Beaver, F.W. A Database of Chemical, Mineralogical, and Physical Properties of Coal Fly Ash—A Research, Utilization, and Disposal Aid. *In Proceedings of the 9th ACAA International Coal Ash Utilization Symposium*; Orlando, FL, Jan 22–25, 1991; Vol. 3, p. 14. Key conclusions from that work were:

- Standard testing applied to coal by-products provides mainly empirical information that is incomplete and can be scientifically misleading as well as misleading in engineering applications and research regarding these highly complex materials.
- Mineralogical characterization of crystalline phases provides a means of identification and quantification. This must be included as a part of a complete characterization scheme for coal by-products in addition to the nominal bulk chemical analyses and physical tests. In addition to these tests, a determination of the leaching characteristics should also be included.
- Chemical interactions between mineralogical phases within the coal by-product or other materials it may contact during utilization are key to understanding the engineering properties and chemical behavior of these materials.
- The scientific experience gained through this study of coal by-products has direct applicability in the development of coal by-products generated from emerging clean coal

technologies. Protocols for the complete characterization of coal conversion solid by-products have been developed and await new materials.

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 results of those tasks were summarized in a report to DOE NETL and CARRC members (“1993–1998 CARRC Final Report”). The tasks described in that report were: 1) the Demonstration of CCB Use in Small Construction Projects, 2) Application of CCSEM (computer-controlled scanning electron microscopy) for Coal Combustion By-Product Characterization, 3) Development of a Procedure to Determine Heat of Hydration for Coal Combustion By-Products, 4) Investigation of the Behavior of High-Calcium Coal Combustion By-Products, 5) Development of an Environmentally Appropriate Leaching Procedure for Coal Combustion By-Products, 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. Key results for 1993–1998 were:

- 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.
- Identification of specific mineral transformations resulting from fly ash hydration.
- 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.

While the initial focus of CARRC was to develop a database of information on coal fly ash, the perspective of members and researchers changed when the CAPD became a research tool and no longer the primary research effort. The success in developing the CAPD through the CARRC team effort provided impetus to expand the activities performed, to include member-driven research tasks that required practical input from members and the technical expertise of CARRC researchers using the available university facilities. CARRC membership has remained relatively constant, with industrial members primarily concerned with the marketing and utilization of moderate- to high-calcium fly ash. These members have facilitated the development of significant information on fly ash chemistry, especially as it relates to the mobility of fly ash constituents on exposure to water, the hydration reactions of moderate- to high-calcium fly ash to improve the understanding of the performance of fly ash in utilization applications, comparative performance of a range of fly ash samples in numerous construction and engineering applications, and the best methods of testing and

analyzing CCBs for accurate and reproducible results that are scientifically valid and legally defensible.

In recent years, an emphasis on information transfer has been added to the CARRC priorities in response to member and industry input. It was evident to CARRC members and researchers that technical reports alone did not meet the need for information dissemination. CARRC researchers needed to present results of CARRC activities in a variety of formats and levels of detail. Many current CARRC technology transfer activities are informal and include providing documents and/or verbal comments to government agencies, end users, citizen groups, students, and other interested parties. The EERC Internet site has encouraged many interactions about CARRC activities and general information on CCBs.

In order to perform research pertinent to CARRC members, members frequently submit samples from their own facilities for inclusion in research tasks. Results of any CARRC tasks are presented in a manner to maintain the confidentiality of CARRC member samples. Each member receives the experimental results based on its submitted materials with appropriate identification, and this courtesy is also offered to nonmembers who contribute samples for any CARRC research. CARRC members may distribute or use any CARRC information as they wish. One example of data confidentiality and distribution is the CAPD, which contains identification and characterization information on more than 800 CCB samples from U.S. and international sources. The majority of the CAPD entries represent member-submitted materials. CARRC members agreed that certain identification fields should only be accessed by the member who submitted the sample. CARRC provides the CAPD to members on computer disks, and each company has its own version of the CAPD that indicates confidential identifying information for that company's samples only. All other fields are available to all users. The CAPD software allows each company to add data to its own CAPD version. Further, each member may distribute copies of its version of the CAPD as desired.

CARRC members and researchers have progressed together technically but have also jointly developed an understanding of the layers of social, regulatory, legal, and competition issues that impact the success of CCB utilization in a generic sense and with regard to specific projects and applications of significance to a single CARRC member. 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 truly successful if it facilitates CCB utilization that meets the performance criteria of the customer. These criteria can include environmental performance, engineering performance, favorable economics, and improved life cycle of products and projects. Members bring to CARRC questions from their daily interactions with customers, end users, and the public. Technical research tasks are developed to address these questions, and members select annual activities by a prioritization ballot. This process limits the number of research tasks annually, but the selected tasks are of highest member priority or need. As stated earlier, CARRC researchers work to make results of technical tasks available to the group or individual who originated the question about CCB utilization.

DOE is a partner in CARRC through the EERC JSRP, which provides matching funds for industrial contributions and increases the level of effort in CARRC. In addition to providing funding, a DOE representative is invited to provide input to technical tasks and other activities. This input is

valuable in providing a broad perspective from a federal agency. CARRC DOE representatives have also indicated that interaction with industry representatives provides perspective that is helpful relative to other DOE project areas and interests. DOE participation has been positive for CARRC and for the CCB industry in general.

CARRC is successful because it provides high-quality, focused research with highly leveraged funds relative to individual industrial contributions. CARRC takes advantage of the diverse experience, knowledge, and skills in its membership and research team and provides a flexible approach to research. CARRC continues to evolve to meet the challenges and needs of its members through high-quality technical research and technology transfer.

CARRC continued research, development, demonstration, and technology transfer focused on the environmentally safe and technically sound utilization of CCBs from 1998 through 2007, and the activities performed, results obtained, and accomplishments for that time period are summarized in this report. Over the duration of 1998 through 2007, CARRC published Annual Reports and Topical Reports for DOE NETL, CARRC members, and special project sponsors. CARRC Annual Reports for 2000 through 2006 are available online at www.undeerc.org/carrc/html/ProgressReports.html. The CARRC Topical Reports published from 1998 to 2007 are listed later in this report.

3.0 OVERALL CARRC RESEARCH OBJECTIVES

The primary objective of CARRC is to work with industry to solve CCB-related technical questions and promote the environmentally safe, technically sound, and economical utilization and disposal of these complex materials. Goals include the generation of scientific and engineering information regarding regulations and specifications for CCBs, the development of improved characterization methods for CCBs, the demonstration of new or improved CCB use applications, and technology transfer.

Activity-specific goals are included in the following discussions of the activities performed from 1998 through 2007. All CARRC activities are designed and performed in order to support the overall CARRC objectives.

4.0 1998–2007 ACCOMPLISHMENTS

CARRC tasks included work to evaluate the physical and engineering performance of CCBs related to use in multiple products; to evaluate and understand the environmental performance of CCBs in a variety of utilization applications and settings; to provide information to CARRC members, government agencies, and other industry stakeholders; and to educate and inform the industry, government, and the public. Most CARRC tasks were performed over multiple years, and some tasks are ongoing.

4.1 Standards Development

The goal of the Standards Development activity was to enhance and promote the technically sound utilization of coal ash through development of technical standard guides or practices for technically proven ash utilization applications. Industry and government identified the development of standards such as this as a key component of efforts to advance the beneficial use of CCPs in the United States.

In 1998–2007, CARRC participated in the standard development activities of ASTM, leading an effort in the ASTM E50 Committee on Sustainable Development and Pollution Prevention.

The previously prepared ASTM standard for the utilization of CCBs for the stabilization of wastes containing hazardous oxyanions was reviewed, and it was determined that the standard would be more useful if it included the solidification of wastes and did not focus on a single stabilization mechanism. CARRC researchers revised the standard and introduced it as “Use of Coal Combustion Products for Stabilization of Inorganic Wastes” under ASTM E50.03 for review and ballot. That standard was approved and reapproved as required after 5 years, with CARRC researchers taking responsibility for all related efforts.

CARRC researchers next developed two standard guides for the use of coal combustion products (CCPs) in surface mines:

- Standard Guide for the Use of Coal Combustion Products (CCPs) for Surface Mine Reclamation and Recontouring and Highwall Reclamation
- Standard Guide for the Use of Coal Combustion Products (CCPs) for Surface Mine Reclamation: Revegetation and Mitigation of Acid Mine Drainage

Both of these standards were approved.

CARRC researchers also worked extensively with other professionals to develop “Standard Terminology for CCPs” and the standard guide on the Use of CCPs in Underground Mine Reclamation.

CARRC researchers also participated in other ASTM committees and subcommittees by voting on appropriate coal ash-related standards.

4.2 Determination of the Rate of Hydration and Reaction Products

The goal of this task was to develop techniques to quantitate coal ash reactivity.

The development and application or modification of analytical and characterization techniques were ongoing efforts in CARRC since its inception. CARRC research highlighted the need for better methods to classify CCBs based on reactivity. Development of new and innovative techniques for quantitating coal ash reactivity and behavior was the focus of investigations. Through the application

of CCSEM and the understanding of the heat of hydration of CCBs, CARRC researchers have worked to develop more reliable and generally applicable predictive capabilities for CCB reactivity. Combining these capabilities with x-ray diffraction (XRD) allowed hydration mechanisms to be better defined. Under this task, multiple fly ash samples were evaluated using a calorimetric method to determine heat of hydration, and these data were incorporated into the CAPD. These data were compared to chemical composition and sample mineralogy. CARRC researchers also continued to evaluate the formation of ettringite, a key secondary hydration product.

In an attempt to incorporate real-world data on long-term performance of fly ash in concrete into this task, engineering performance tests were performed on high-volume fly ash concrete (up to 70 % fly ash as the cementitious material). The concrete samples evaluated were from sites where CARRC researchers had good data on the fly ash used, the mix designs, and the placement techniques. These data were used to facilitate a preliminary attempt to develop an improved classification system for CCBs under this task. The concept for the new classification system was to develop a 2-number system where one number would indicate the level of pozzolanicity of the material and the second number would provide an indication of the cementitious level of the sample. It was determined that the analytical methods to develop this two-tiered system required further refinement, and further work was replaced by higher-priority activities.

4.3 Assembly of NORM Data on CCBs

This work task was developed to provide CARRC with scientifically valid data that could be used to formulate an appropriate response to nontechnical groups concerned with the issue of naturally occurring radioactive material (NORM) on CCBs.

The presence of NORM on CCBs has historically been an emotionally charged issue for citizen's groups and regulatory agencies. Sound scientific information on the NORM content of CCBs has not been readily available in the literature, so the issue has been difficult to abate from a technical standpoint. Three subtasks were performed:

- NORM terminology, definitions, and baseline information was assembled
- A set of 38 ash samples was analyzed for isotopic constituents (isotopes included were ^{210}Pb , ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{234}Th , ^{212}Pb , and uranium)
- Radon emanation studies were performed on coal ash, soil, and cement samples.

A CARRC topical report entitled "Naturally Occurring Radioactive Materials in Coal Combustion By-Products," including the information assembled, was prepared and distributed to CARRC members.

4.4 Mercury Issues Related to CCB Utilization

This task was selected by CARRC members to facilitate development of data on mercury and CCBs.

This work task was undertaken by CARRC, in cooperation with multiple efforts at the EERC, to develop a comprehensive database of the mercury content of CCBs in samples representing a variety of coal–fuel sources, combustion systems, emission control systems, and mercury content in order to obtain more detailed information on the potential for environmental release including speciation. The work under this task included:

- Collection of CCB samples from CARRC members and other groups.
- Determination of total mercury content.
- Application of leaching methods to CCB samples.
- Development of a laboratory method to determine vapor-phase mercury releases on exposure to elevated temperatures and application to CCBs samples.
- Long-term experiments to determine mercury release from CCBs at ambient temperature.
- Development of laboratory methods to determine the impact of microbial activity on the leaching and vapor-phase release of mercury and application to CCBs.

4.4.1 Methods

A detailed description of methods used can be found in the EERC report to DOE NETL entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization”. (1)

Leaching was carried out with the synthetic groundwater leaching procedure (SGLP) leaching protocol using distilled deionized water as the leaching solution, including long-term leaching (LTL). Toxicity characteristic leaching procedure (TCLP) was also applied to some samples.

Samples of mercury and mercury compounds for controlled thermal desorption were placed in quartz with minimal packing to avoid excessive pressure drops across the sample mass. Based on the mercury concentration of the sample, the mass of sample used for each test was sufficient to provide 100 to 250 ng of mercury, typically requiring <1-gram samples for the ash. Replicate samples were run because it was often necessary to make adjustments to sample mass and sensitivity settings to obtain statistically significant thermal desorption results. The release of mercury from coal fly ash into the atmosphere was also of interest to CARRC members, so an effort was initiated to evaluate desorption at elevated, ambient, and temperatures just above ambient (~40°C). Thermal desorption was evaluated at up to 600°C, and resulting data showed a variety of desorption curves ranging from mercury measured at a single peak to four mercury peaks for a single sample. While it was hypothesized that desorption temperatures would provide information on the mercury species in the ashes evaluated, results did not correlate with published data on volatility temperatures for mercury compounds. Work continues on thermal desorption of mercury with an improved apparatus capable of evaluating thermal desorption at temperatures up to and just above 600°C.

Long-term experiments to determine mercury release from CCBs at ambient temperature were also performed. Mercury-free air was passed through 100-gram samples of select fly ash samples submitted by CARRC members. Preliminary results indicated that some samples emitted as much as 200 pg of mercury during the first 90-day collection period. These experiments continue, and CARRC researchers will provide results to CARRC members at upcoming meetings. This particular project has been extremely challenging and has resulted in protocols for desorbing and measuring mercury vapor at extremely low concentrations. This work continues with development of an improved desorption apparatus as well as with work on the effects of biological activity on mercury release from CCBs. Mercury release was quantitated at 90-day intervals for 9 months. Preliminary results indicated that mercury release at ambient temperatures is extremely low. When these results are applied to a coal-fired power plant producing 200,000 tons of fly ash annually, it would imply that that plant could potentially release 0.0006 pounds, or 0.26 grams, of mercury annually from its fly ash.

Microbiological releases were evaluated using two different approaches. The first experimental design used mixtures of the CCB with a buffered solution and addition of a mixed bacterial culture in a shaken or stirred container. Analytical traps were used to capture mercury released in the vapor phase, and after the experiment was completed, mercury was determined in the solution to evaluate the microbiologically mediated mercury leaching. This experimental design worked well for CCBs with near-neutral pH; however, it was not readily adapted to samples with high pH as it was not possible to maintain the pH in a range conducive to support the viability of bacteria. An alternate experimental design was developed in which moist CCB–soil samples were placed in containers that allowed the evaluation of vapor-phase mercury releases, similar to the long-term ambient temperature vapor-phase mercury release determinations.

4.4.2 Results and Conclusions

Results and conclusions of the work performed through CARRC and the information assembled for CARRC members can be summarized as follows:

- Laboratory methods were developed to evaluate the potential for mercury releases under several release mechanisms.
- Mercury was not readily leached from fly ash or flue gas desulfurization (FGD) materials, and mercury leachate concentrations did not correlate to total mercury concentrations. Leachate concentrations for most samples fell below the primary drinking water limit of 0.02 µg/L.
- Most samples acted as mercury sinks in ambient-temperature vapor-phase release experiments.
- Organomercury compounds were present in leachates from microbiological experiments.
- Some vapor-phase mercury from microbiological experiments showed evidence of methylation.

- For comparative baseline and test samples containing activated carbon (AC), total mercury content was higher in the test samples, and elevated concentrations of selenium were noted in some samples.
- Many fly ash samples, and especially those with unburned or AC present, sorb mercury in ambient-temperature vapor-phase experiments. When releases were noted, they were extremely low both in total released over extended laboratory tests and in rate released.
- Under microbiologically mediated conditions, elemental and organomercury were released both to the vapor phase and the leachate but only at very low levels. While the levels of elemental and organomercury were low in both leachate and vapor, more elemental mercury was released. Very low amounts of elemental and organomercury releases were measured from soil–CCB mixtures in simulated field experiments. The results were consistent between the two experimental designs.
- Microbiologically mediated vapor-phase mercury releases were the most challenging to carry out. Limited data indicated the potential for increased elemental mercury and organomercury release when fly ash was mixed with soil compared to releases from fly ash alone.

4.5 Evaluation of Fly Ash and Fly Ash–Sorbent Blends for Mercury Release and Utilization Potential

In related work and using data from CARRC and other EERC efforts, CARRC researchers worked to assess the impacts of AC on the utilization of fly ash. The results of this review are as follows.

Fly Ash Utilization in Concrete – Laboratory foam index testing at the EERC and elsewhere has shown that AC, even in very small percentages, can have a drastic effect on the amount of air-entraining agent (AEA) required to produce sustainable foam in cement–fly ash mixtures. Based on EERC experiments to evaluate mercury releases from fly ash and fly ash + AC, the potential for mercury to be released from the fly ash in concrete mixing, placement, and use is very low. Release of mercury from concrete that is recycled or disposed of in construction landfills should be similarly low.

Geotechnical Applications (structural fills, embankments, mining applications, and soil stabilization) – For fly ash + AC (injected before the primary collection device), the physical and engineering performance of the material is expected to be similar to that of the associated baseline fly ash, with some potential for handling issues such as increased dusting. The presence of AC is not expected to affect the pozzolanic/cementitious performance of the fly ash. Laboratory results indicate that release of mercury through leaching, exposure to ambient temperatures, and microbiologically mediated release will be very low and should not preclude the use of fly ash + AC in these applications.

Cement Manufacture – Laboratory experiments indicated that for almost all fly ash and fly ash + AC samples, 100% of the mercury was released by the time the sample had reached 750°C (1382°F). Since cement kilns reach temperatures significantly higher than the experimental maximum, it is expected that the mercury associated with fly ash + AC would be released during the clinker formation process. This may not mean that, however, all the mercury would not be emitted to the atmosphere because the operation of the kiln could result in some of the vapor-phase mercury being captured in existing emission control devices.

Waste Stabilization and Solidification – Because of the variety of wastes that may be stabilized or solidified with fly ash, it is not possible to discuss the physical performance or potential mercury release for fly ash + AC except to indicate that the pozzolanic/cementitious performance is not expected to be impacted by the presence of the AC.

4.6 The Use of CCBs in the Management of Feedlot Wastes

Odor control, waste management, and animal comfort at feedlot operations are of concern throughout the United States. Based on performance in other use applications, CCBs have great potential in the abatement of odor, waste management, and improved animal comfort. CARRC performed a literature search to collect, evaluate, and summarize current information on CCB projects in this area. The literature search was completed on the use of ash in feedlot applications. A visit was made to ash-surfaced feedlots in Ohio in conjunction with a field trip for the American Coal Ash Association (ACAA) meeting in June 1999. Discussions were initiated with various relevant organizations to supplement the written documentation gathered. An annotated bibliography was published entitled “Feedlot Stabilization Using Coal Combustion By-Products.” The bibliography features over 50 entries and highlights topics in the areas of ash components, environmental evaluation tools, surfacing technologies, the relationship between animal health and ash use, odor control, and the effect of ash-animal waste mixtures on soil quality. A follow-on project was developed to demonstrate the use of CCBs in feedlot settings in North Dakota. Although not a CARRC effort, CARRC members were provided the opportunity to follow the project, and the final report “Demonstration of Coal Ash for Feedlot Surfaces” was made available to them.

4.7 Technical Evaluation of Rammed-Earth Building Products

A demonstration of rammed-earth (RE) building construction was proposed in North Dakota. RE construction is a method of construction using earth compressed into a form, similar to adobe. There is renewed interest in RE construction in part because of the rising cost of traditional wood building materials and the increased awareness of energy-efficient materials. Some soils are appropriate for RE construction without the use of additives as stabilizers; however, more frequently, soils need some amendment to meet performance requirements for durability and strength. Coal combustion fly ash and bottom ash have excellent potential for use in RE construction as low-cost alternatives to portland cement and other stabilizers because of their cementitious properties. This task was developed as a CARRC special project to evaluate the end product of the RE process for performance and durability.

CARRC investigated the use of fly ash and bottom ash from a North Dakota lignite-fired power plant for use as a soil amendment for RE construction. Extensive evaluations of North Dakota lignite ash for environmental suitability, physical properties, and engineering performance indicate that lignite fly ash is environmentally benign and offers advantageous cementitious performance. Lignite bottom ash is also environmentally benign and has properties similar to the aggregate used in numerous applications. Ash-containing RE demonstration products using the North Dakota soils and ash proposed were produced and evaluated in the laboratory for strength, durability, and insulating/thermal properties. A practical review of the RE technology and an evaluation of market potential for RE buildings in North Dakota and the region were also performed. The results of this effort indicated that coal fly ash and bottom ash can be used in RE construction, and the ash–earth mixture needs to be evaluated based on the specific soil and ash to be used. While the effort indicated that RE is not expected to be widely used in North Dakota, it indicated that, in other locations, bottom ash may be an option for modifying the soil to produce a better RE product and may improve the insulative properties of RE walls. Reactive fly ash was found to be a good candidate to add strength to RE and was recommended as an environmentally friendly option where a cementitious additive is required to achieve soil strengths for RE construction. A CARRC topical report entitled “The Use of Bottom Ash and Fly Ash in Rammed-Earth Construction” was prepared and submitted to CARRC members.

4.8 CCBs from Combustion of Coal with Other Fuels

Combustion of biomass fuels either alone or in conjunction with coal has the potential to result in by-products with different characteristics than 100% coal or other fossil fuels. Coal–biomass by-products are expected to be appropriate for some utilization applications, but the primary issue of cocombustion of biomass with coal relates to fly ash use as a mineral admixture in concrete. ASTM had an existing standard specification for 100% coal fly ash for use in concrete (C618) even though some coal–biomass fly ash had been shown to meet the technical specifications noted in this standard. One key difficulty was that the definition of fly ash in the standard indicates that it refers to fly ash produced only from 100% coal as the fuel.

CARRC researchers worked with other EERC researchers to develop technical data on fly ash samples produced from the cocombustion of coal and biomass. A limited number of coal–biomass ash samples were evaluated in the laboratory for key properties that are important in facilitating by-product management decisions, especially as they relate to use in concrete. In addition, a database of the characterization data from this effort and other EERC efforts was developed, modeled after the CARRC CAPD.

Fly ash samples were collected from the EERC’s conversion and environmental process simulator (CEPS) combustor and analyzed using a CCSEM method of analysis that generates particle size, shape, and chemical information on thousands of particles per sample. A Powder River Basin subbituminous coal and an eastern bituminous coal were selected as the coal types. The biomass fuels selected were alfalfa stems, wheat straw, and hybrid poplar. Baghouse ash from each of these fuels and 80% coal and 20% biomass blends for each combination were collected and analyzed. Multivariate analysis, specifically cluster analysis, was performed on each of the samples, and comparisons were made between the coal ash, biomass ash, and blended fuel ash. Biomass ashes

and the cofired fuel ashes tended to have significant amounts of K, S, and Cl, which are often detrimental to any beneficial use applications. Initial results indicate that these elements may be in the form of salts (K_2SO_4 and KCl) and are likely adhering to the surface of the ash particles. Potassium is also incorporated into the amorphous silica glass in small amounts. Thermal desorption was also performed on selected samples over a temperature range from ambient to 600°C.

The data were compiled and are available on the ABC Database on www.undeerc.org/carrc/html/Databases.html.

4.9 Buyer's Guide to Coal Ash-Containing Products

In order to emphasize the commercial availability of consumer construction products containing CCBs, CARRC developed the "Buyer's Guide to Coal-Ash Containing Products."

The Buyer's Guide was targeted toward buyers who included contractors and consumers seeking environmentally friendly products. The first version of the Buyer's Guide was prepared as a hard copy that could be provided to interested parties. The document discussed the commercial uses of four specific CCBs: fly ash, bottom ash, boiler slag, and flue gas desulfurization material. The Buyer's Guide included products in the areas of agriculture, building materials, cement and concrete, civil engineering, and specialty materials, as well as others. Along with product listings, the Buyer's Guide also emphasized the recycling aspects of CCB utilization. Each product listed contains coal by-products and is commercially available on the market.

Achieving mass distribution was the primary goal for the Buyer's Guide so follow on efforts were made to make the Buyer's Guide available to a broader audience by producing an searchable Web-based version which is currently available on <http://www.undeerc.org/carrc/html/Databases.html>. The Buyer's Guide was also made available on CD-ROM for distribution to CARRC members and other interested parties. The current Web-based version allows instant updates and features approximately 80 products and an improved cement and concrete section.

4.10 Development of Beneficial Use Policy for Bottom Ash

In an effort to develop information that will facilitate the development of a beneficial use policy for bottom ash by the Wyoming Department of Environmental Quality (DEQ), CARRC researchers performed several tasks:

- Assembly of information to explain the properties of bottom ash, including environmental performance data.
- Development of conceptual models addressing how the product is expected to perform environmentally under specific applications.
- Assisting the Wyoming DEQ in developing a list of preapproved applications for bottom ash.

CARRC researchers worked with the Wyoming DEQ staff to assemble information on regional bottom ash, presented a workshop to Wyoming DEQ staff, and prepared multiple options of outlines for bottom ash beneficial use guidance.

4.11 Evaluation of Coal Fly Ash Variability

An evaluation of variability of coal fly ash from several coal-fired power stations in North Dakota, South Dakota, Wisconsin, and Iowa was performed with the goal of enhancing the CAPD and to develop an improved understanding of the inherent variability associated with fly ash and the commonly applied test procedures. Three to five fly ash samples were collected from a limited number of power stations and evaluated for ASTM C618 parameters. Data were subjected to statistical analysis. Standard deviation was the primary statistical tool used to estimate the probability that a single test result may have incorrectly indicated that a fly ash does not meet a particular specification. Results indicated that statistical variability was low for samples from a single source.

4.12 Comparison of Available Swell/Expansion Tests and Development of an Expansion Test for CCBs

Swelling or expansion of products containing CCBs has occurred in cases where standard tests have not indicated potential for expansion. CARRC proposed to evaluate standard expansion tests and to identify suitable tests for CCBs or soil-CCB mixtures.

ASTM test methods for swell/expansion were identified and reviewed. It was concluded that the expansion test methods are very similar in practice and that none were developed with consideration for the composition or properties of CCBs. Some tests have been modified for use with varying materials, and increased time was recommended in some instances for use in evaluating CCBs in an attempt to allow the formation of ettringite and other hydrated phases that can lead to expansion; however, a CCB-specific test is not listed by ASTM. Based on review of the existing tests and modifications and the anecdotal evidence of expansion at sites where CCBs were used after passing standard tests, it was concluded that a simple comparison of laboratory results from existing tests would be inadequate. The task proceeded with design of an alternative method for determining swell and expansion. The method was based on material density using the hypothesis for the method development that the density of CCBs pre- and postexpansion would differ. It was proposed that a reduction in density in the hydrated sample can be related to swell potential based on proposed expansion mechanisms. A reduction in density would relate to expansion because of hydration of the sample. Densities of material suspected of having swell potential were determined using ASTM C 188-89 Standard Test Method for Density of Hydraulic Cement commonly used for fly ash. The same material is hydrated over a time period from 30 to 60 days. A timed hydration series was also performed on a single ash sample, with the sample being hydrated for 2, 4, 8, and 13 weeks to further evaluate the density changes and determine the potential for this draft method to predict potential for expansion. XRD was used to identify the starting mineralogy of the pre- and posthydration samples in order to determine if expansive hydration reactions had occurred. Following hydration, the sample was dried at 55°C and retested. This temperature was chosen because it has been found that, at 55°C, ettringite does not lose water of hydration and retains its crystalline integrity. The single operator standard deviation for this test is reported to be 0.012, with a difference of not more than 0.03%.

This is much greater accuracy and precision than would be needed to identify changes that were expected to relate to expansion. Results indicated that changes in density can be used to predict potential for expansion in dry powdered materials such as CCBs. The method is currently being used in research projects, and opportunities for validation are being explored.

4.13 Handling and Use of Wet and Dry FGD Material

Annual production of FGD material is projected to increase significantly as proposed regulations related to coal-fired power plant emissions result in the increased installation of FGD systems. This production increase, coupled with future federal guidance on the disposal and mine placement of CCBs, including FGD material, is expected to have a significant impact on utility CCB managers and others involved in CCB management. The Utility Solid Waste Activities Group provided funding for a CARRC special project to develop baseline information related to the character and management of FGD material. Literature searches were preformed, and CARRC members provided information on existing FGD materials and management practices. A topical report entitled “Review of Handling and Use of Wet and Dry FGD Materials” was prepared for CARRC members. The report included information on the state of the FGD production; a review of various FGD systems; and current practices for handling, disposing of, and utilizing these materials. This effort resulted in identification of a need for information on wet nonoxidized and dry sulfite-rich FGD materials.

4.14 Utilization of Sulfite-Rich FGD Material

A CARRC research task was formed to develop additional information on calcium-based FGD materials that contain significant levels of calcium sulfite as compared to calcium sulfate (gypsum). This task focused on wet nonoxidized FGD material (from systems referred to as inhibited or natural oxidation) and spray dryer absorber materials. Several technical questions were raised in previous CARRC tasks and other EERC research efforts:

- What is the bulk composition of the various sample types, and what is the range of sulfite/sulfate ratios in the samples?
- At what rate does sulfite oxidize to sulfate?
- What conditions facilitate conversion of sulfite to sulfate?
- What is the physical impact of the oxidation if it occurs in a manufactured product?

A sample set of sulfite-rich FGD were subjected to laboratory evaluations. The chemical variability of sulfite-rich FGD materials was determined through chemical characterization tests. Sulfate–sulfite ratios were determined and limitations to the existing laboratory methods were identified. Expansion, strength testing (cement pozzolanic activity), and bulk major chemistry were completed on a subset of samples. Results indicated chemical composition variability between the varying samples types as expected, but the engineering performance tests provided the most interesting results. Strength development tests indicated that all samples met the maximum water

requirement limit, but only one sample, an FGD–SDA (spray dryer absorber) material, achieved adequate strength at 28 days to meet the strength activity index specification. All samples exhibited expansion, and evaluation of sulfite oxidation indicated that the rate of oxidation is variable. Results of the testing indicated that SDA materials showed good potential for use in cementitious applications but that additional work would be required to address performance questions related to material variability.

4.15 Review of Literature on Spray Dryer Absorber Material

As a follow-on to the laboratory evaluations of sulfite-rich FGD materials, CARRC researchers initiated a special project to assemble information on SDA materials worldwide, including the range of material composition and behavior and utilization applications for SDA materials.

The literature search, interpretation, and information assembly focused on calcium-based SDA materials. It was found that in the United States, SDA systems typically collect fly ash (40%–75%) and sorbent together, taking advantage of the alkalinity of fly ash and its sulfur dioxide sorbent capabilities resulting in compositional variability which was demonstrated by data from the literature review and laboratory work done by CARRC researchers. Physical properties and performance also varied significantly.

In the literature reviewed, a number of current commercial and potential uses of SDA material were identified, including agriculture, binders, cement manufacture, cement replacement in concrete, civil engineering, flowable fill, fixating agent for waste, marine applications, masonry, mineral wool, mining applications, soil stabilization, sulfuric acid production, synthetic aggregate, wallboard, and wet FGD sorbent. Many of the commercial uses are being implemented successfully in Europe but are slower to enter the marketplace in the United States. Potential uses in the research and development stage were rated as high-, moderate-, or low-potential commercial applications. High-potential applications for the U.S. market are estimated to be those that take advantage of the presence of the fly ash component of the SDA material, can tolerate relatively high sulfur content, and have limited susceptibility to expansion or reduce expansion potential in the production process. These applications fall into two categories: 1) cementitious products and 2) mining applications. The need for utilization options of SDA materials in the United States is expected to increase as the use of SDA systems is expected to grow over the next 10 years. A topical report entitled “A Review of Literature Related to the Use of Spray Dryer Absorber Material: Production, Characterization, Utilization Applications, Barriers, and Recommendations” was prepared for CARRC members in October 2007.

4.16 Environmental Performance of CCBs

Environmental performance of CCBs was identified as a technical issue that needed to be addressed early in CAARC work. A general task to evaluate environmental performance of materials for CARRC members and CARRC tasks was initiated with the goal to provide sound data to CARRC members and industry stakeholders. Initial work was performed to evaluate a variety of CCBs using chemical and mineralogical characterization techniques. Materials were then subjected to leaching tests, and the mineralogy of the hydrated samples was determined in order to better

understand the hydration mechanisms and the impact to leaching characteristics. Data were assembled for CARRC members and reported to members at annual meetings; incorporated into the CAPD; and used to respond to requests from members, government agencies, users and other stakeholders. Based on the work performed, it was recommended that additional work on development of leaching procedures be performed. A follow-on task to work with DOE NETL to compare results of several commonly applied leaching procedures was proposed to members.

4.17 Evaluation of Current Leaching Procedures

The goal of this task was to work with other organizations to perform an informal interlaboratory comparison of common leaching techniques.

Leaching of CCBs using various batch laboratory methods has been performed under numerous CARRC and EERC projects, and it was determined that some common leaching methods were not scientifically sound and did not produce valid data. Other research groups and government agencies have also begun to agree that existing leaching methods are not appropriate for CCBs, and discussions were initiated that raised questions regarding which leaching methods are appropriate and how to determine their appropriateness. As a result of these discussions, CARRC researchers and several other laboratories participated in a DOE NETL-led interlaboratory comparison of four leaching tests, including SGLP and LTL. CARRC initiated its evaluation using two fly ash samples with different characteristics. Results of all laboratory efforts were shared with all participants, and CARRC results were included in a paper presented by the DOE NETL researchers.

In associated work evaluating leaching profiles for fly ash-AC samples, CARRC researchers identified interesting pH development phenomena that were further investigated under CARRC. Since the pH of a material influences the leaching profile, CARRC researchers performed pH measurements with several different protocols in order to provide information that was expected to aid in identifying appropriate leaching tests and conditions. Significant increases in pH were noted for lignite and bituminous fly ash-AC samples between readings taken at 10–15 minutes and at 24 hours. Significant decreases were also noted for some samples of bituminous fly ash. Results of this activity suggested that leaching methods imposing a specific pH in a CCB leaching system may not be providing the information that has been expected.

The CARRC effort continues with both laboratory evaluations and discussion of appropriate environmental characterization with various groups. Results from this study are expected to be valuable in the CARRC-led ASTM effort to develop a standard method to identify appropriate leaching procedures for industrial by-products.

4.18 Characterization of Ammoniated Ash

A CARRC special project was developed to better understand the impacts of ammonia on fly ash related to its environmental performance. The task had two activities: 1) a literature review and 2) a laboratory evaluation of leaching of ammoniated ash samples.

CARRC completed the first phase of this task by assembling technical documentation on ammoniated coal fly ash and technologies that produce ammoniated coal fly ash. These publications were evaluated and are summarized in an annotated bibliography entitled “Ammoniated Ash.” The bibliography features over 30 entries and highlights topics in the areas of selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), NO_x control, utilization, disposal, slip, and regulations. Based on the literature search, it was determined that a limited amount of research has been conducted on the performance of ammonia-contaminated ash when used as a mineral admixture in concrete. The bibliography was published for CARRC members.

CARRC researchers used laboratory evaluations to determine the potential environmental behavior of ammoniated ash under a variety of conditions. The experiments included batch, sequential, and column leaching and an evaluation of the effect of biota on leaching of ammoniated ash. Samples, provided by CARRC members, were an alkaline ash, an acidic ash, an aged landfilled ash, and soil. Experiments focused on the acidic ash, which was ammoniated at three levels in the laboratory. The leachates and solid samples were analyzed for pH, ammonium, nitrite, nitrate, sulfate, and trace elements. Ammonia was detected in leachates from most samples, as anticipated. While nitrate was present in leachates from ash samples obtained from an ash landfill, nitrite was not present, consistent with the rapid oxidation of nitrite in aqueous conditions. The presence of ammonia does impact the leaching profile of some trace elements, including arsenic, fluorine, molybdenum, nickel, and zinc.

CARRC focused its efforts on a laboratory evaluation of the behavior of ammonia and other nitrogen species when ammoniated ash is exposed to water and of the impact of ammonia on the leaching and attenuation of trace elements in fly ash. Several ash samples were used in leaching experiments and offgassing evaluations. Results of leaching experiments indicated that leachate pH increased with increased ammonia and constituents tested exhibited one of three types of leaching behavior. Constituents in the first group—ammonia, arsenic, fluoride, molybdenum, selenium, and vanadium—showed increasing leachate concentrations with increasing ammonia concentrations in the fly ash. Constituents in the second group—boron, bromine, chlorine, and sulfate—were unaffected by the increased ammonia concentrations. Constituents in the third group—cadmium, nickel, and zinc—showed decreasing leachate concentrations with increasing ammonia concentrations in the fly ash. Results also indicated that the constituents that showed increased leaching with increased ammonia content were highly attenuated by soil. Results from this task indicated that the introduction of ammonia to ash will impact the leachability of various constituents present in the coal ash. A topical report entitled “The Impact of Ammonia on the Leaching of Selected Constituents from Coal Fly Ash” was submitted to CARRC members.

4.19 Sediment Attenuation Effects on Coal Ash Leachates

At coal ash disposal sites, measurements of groundwater quality are usually made at a compliance boundary, a point where the leachate has passed through soils and components have been attenuated and potentially diluted. The compliance boundary typically identifies the point where the leachate from a material is considered to have entered the environment. Sites where coal ash is utilized do not have designated compliance boundaries, so tools are needed to assess the impact of coal ash leachate to the environment. This task was developed to determine the impacts of contact

with sediments on leachate generated from CCBs. In testing on specific sediments submitted by CARRC members, partitioning of leached constituents between the aqueous phase and the solid phase was evaluated. Trace elements included in the laboratory experiments were arsenic, boron, cadmium, chromium, mercury, lead, nickel, and selenium.

The distribution coefficients (K_d) were determined for selected sediments for each element. Most elements were either highly or moderately attenuated. In acid-forming sediments as might be found in some mine settings, this initial attenuation could be reversed by the formation of strong acid. The determination of K_d will allow for the evaluation of subsurface transport of trace elements, and work to accomplish this will continue.

4.20 FlexCrete™ Feasibility Study

A special project was performed to assess the feasibility of building a FlexCrete™ manufacturing facility on the reservation in Belcourt, North Dakota. FlexCrete™ is an aerated concrete building material developed by Headwaters Resources using fly ash as a primary raw material. A critical review of FlexCrete™ characteristics and potential regional markets indicated that this product would offer advantages related to energy efficiency and sustainability.

4.21 Freeze–Thaw Study

Freeze–thaw performance of concrete is important throughout the United States, and the evaluation of this parameter requires specialized equipment and experienced technicians. CARRC performed testing to determine the freeze–thaw characteristics of fly ash concrete and a proprietary fly ash-based sprayed coating as special projects.

In the first project, seven concrete mixes were evaluated using ASTM Standard Method C666. The beams were so arranged that, except for necessary supports, each specimen was completely surrounded by water at all times while being subjected to freezing and thawing cycles. Measurements taken included length (in.), weight (lb), and transverse frequency (Hz). Calculations performed included percent change in length and weight, relative dynamic modulus (RDM), Young's modulus of elasticity, and durability factor. Generally, the RDM, which is an indication of the internal condition of the concrete, is preferred to be higher than 70%–75%. Using the RDM as a criterion, the concrete specimens here appear to have satisfactorily endured the rapid freezing and thawing action. The RDM in all cases was over 80%, with length expansions varying between –0.067% and 0.133%. The results from this task were included in the CAPD.

In the second effort, several sections of coated wood utility poles were subjected to the same test as noted above. Results indicated that the coating required further refinement prior to use for utility poles in environments where exposure to freeze–thaw conditions was expected.

4.22 Education and Training

4.22.1 Workshops and Training Courses

CARRC researchers developed and presented workshops and short courses on specific topics of interest to CARRC membership, government, and related industries. In 1998, CARRC researchers developed a Coal Combustion By-Product Utilization Workshop focused on promoting the use of CCBs and understanding their physical and chemical characteristics and use applications. The workshop was directed at environmental specialists, architects and engineers, government agency representatives, construction contractors, and utility personnel. The CCB Workshop was presented in Orlando, Florida, in January 1999, in conjunction with the ACAA 13th International Symposium on the Management and Use of Coal Combustion Products. As a result of discussions during and after presentation of the CCB Workshop, CARRC researchers developed a workshop focused entirely on environmental issues for state agency representatives. The 1-day workshop, entitled “Environmental Aspects of Coal Combustion By-Products Production and Management,” was first presented to representatives of the Wyoming Department of Environmental Quality in Casper, Wyoming, in February 1999.

In 1998, the Western Region Ash Group (WRAG), ACAA, the DOE Federal Energy Technology Center, the University of Wisconsin-Milwaukee, Pozzolanic Northwest Inc., National Minerals Corporation LaFarge, and Boral Material Technologies Inc. asked CARRC researchers to organize a workshop on using CCBs in public works. The result was the WRAG Interactive Forum on Utilization of Coal Combustion By-Products in Public Works, which was held in Salt Lake City, Utah, in April 1998. A follow-up to the forum, the second Annual WRAG Forum: Coal Combustion Product Utilization and Mining Applications, was held in Scottsdale, Arizona, in August 1999, in conjunction with the 16th American Society for Surface Mining and Reclamation National Conference.

In 2004, CARRC organized its first Coal Ash Professionals Training Course (CAPTC), held May 10–13, 2004, in Bloomington, Minnesota. The attendance of 63 people comprised ash managers at electric generating companies, sales and technical staff at ash marketing companies, and representatives of research and academia. Presentations included discussions of the fundamentals of coal ash formation and ash handling, impacts of emission controls, and existing and future markets for coal ash. The course was very well received, and attendees particularly enjoyed the classroom-style learning experience coupled with networking opportunities offered by sponsors, such as tickets to a Twins baseball game.

The second CAPTC was held April 19–21, 2006, in Memphis, Tennessee. With 85 attendees from 31 states and three Canadian provinces, the CAPTC was an enormous success and well supported by industry sponsorships. Attendees learned the fundamentals of the coal ash business, including characterization, management, and utilization and even attended a Memphis Redbirds baseball game.

A third CAPTC will be March 11–13, 2008, in San Antonio, Texas. It is anticipated that subsequent CAPTCs will be held at various locations throughout the United States every 2 years.

At the request of a CARRC member, CARRC conducted a course specifically targeted toward science teachers on June 6–7, 2005, in Washburn, North Dakota. The premise of the course was to get educators thinking about what happens to the by-products after coal is burned to generate electricity. The course included lectures, science experiments, and a tour of Great River Energy's (GRE's) Coal Creek Station Power Plant. The course was attended by 20 people from North Dakota and Minnesota. Based on the feedback received from the course evaluation forms, the teachers were surprised at how valuable the course was. One attendee noted that the course "really got me thinking about information I knew very little about." Another said, "Seeing and hearing the possible (energy) prospects for our state is important—we need to pass on our knowledge." This in-person workshop laid the foundation for the development of the online course "Coal Ash in the Classroom" by CARRC.

4.22.2 Electronic and Internet-Based Resources

4.22.2.1 Coal Ash in the Classroom

The EERC with the UND's Division of Continuing Education launched "Coal Ash in the Classroom," an interactive online course designed to take people behind the scenes of the coal-fired power plant industry to learn what happens to the by-products. The course offers a unique blend of geography, chemistry, and engineering. Students learn from and participate in self-checks, video/audio and text-based lectures, quizzes, animation, and graphical elements.

The course was originally designed to offer educators continuing education credits; however, several professionals in the coal ash industry, including regulators, ash managers, and ash marketers, have taken the course. As of December 2007, 27 people have taken the course. It is anticipated the course will remain active until 2009, at which time it will be reevaluated.

4.22.2.2 Coal Ash Resource Center Web Site

In 2001, a revised Coal Ash Resource Center Web site was developed with the aim to educate both technical and nontechnical audiences about CCBs. At the time, the site was said to be "the most comprehensive site related to coal ash on the Web."

In order to increase site traffic, a promotional campaign was launched in 2001. Over 300 professionals active in the ash industry along with coal ash-related research institutions, organizations, and government agencies were contacted via e-mail inviting them to visit the innovative site at www.undeerc.org/carrc. The campaign also included a link-exchange program, where various coal ash-related sites were listed on the CARRC site in exchange for a listing on their sites.

Since its original creation, site content has been continually updated with new technical reports, CARRC Annual Progress Reports, and databases including the Buyer's Guide to Coal-Ash Containing Products, the FIRST SEARCH document database, and the ABC Database.

4.22.2.3 Coal Ash Properties Database

Data from over 900 samples dating back to 1981 from the original CAPD were incorporated into a new Microsoft Access database. This new format allows users to access and manipulate data in a universal program. Querying the data to formulate forms and reports is now simpler and faster, facilitating CARRC research efforts.

4.22.2.4 Ash from Biomass and Coal (ABC Database)

Funded by the Center for Biomass Utilization®, the ABC Database comprises data collected from over 80 different samples, including coal–biomass fuels, coal, biomass, and ash from fuel and fuel blends. The data held in ABC are very similar to that in the CAPD. The ABC Database is an Access database, and queries were developed to create relationships between data. A menu-driven system for navigation was also implemented to make the database more user-friendly and searching the database easier.

4.23 Research Exchange

CARRC researchers have presented and published their work via numerous conferences, symposia, workshops, and peer-reviewed publications throughout the year, affording CARRC the opportunity to showcase its research regionally, nationally, and internationally. In turn, these exchanges keep CARRC on the cutting edge of research and technology and bring new members into the consortium.

4.23.1 CARRC Topical Reports

CARRC topical reports were prepared on several completed tasks:

- The Impact of Ammonia on the Leaching of Selected Constituents from Coal Fly Ash
- Review of Handling and Use of Wet and Dry FGD Materials
- Use of Fly Ash and Bottom Ash in Rammed-Earth Construction
- Comparison of Dry Scrubber and Class C Fly Ash in Controlled Low-Strength Materials (CLSM) Applications
- Evaluation of Variability of Coal Fly Ash from Midwestern Utilities
- Feedlot Stabilization Using Coal Combustion By-Products: An Annotated Bibliography
- Buyer's Guide to Coal Ash-Containing Products
- Turtle Mountain Band of Chippewa Flexcrete™ Production Market Feasibility Study

- Naturally Occurring Radioactive Materials in Coal Combustion By-Products

4.23.2 Technology Transfer

The following is a list of technical papers and presentations related to CARRC work by year.

1998

Dockter, B.A. Comparison of Dry Scrubber and Class C Fly Ash in Controlled Low-Strength Materials (CLSM) Applications. In *The Design and Application of Controlled Low-Strength Materials (Flowable Fill)*, ASTM STP 1331; Howard, A.K.; Hitch, J.L., Eds.; American Society for Testing and Materials: 1998; pp 13–26.

Dockter, B.A. *Evaluation of Variability of Coal Fly Ash from Midwestern Utilities*; Final Report for Environmental Resource Corporation; EERC Publication 98-EERC-02-03; Energy & Environmental Research Center: Grand Forks, ND, Feb 1998.

Hassett, D.J. Ettringite Formation as a Fixation Technology for Immobilizing Trace Elements. Presented at the 15th Czech and Slovak Conference on Clay Mineralogy and Petrology, Brno, Czech Republic, Sept 6–10, 1998.

Hassett, D.J. The Synthetic Groundwater Leaching Procedure. In *Encyclopedia of Environmental Analysis and Remediation*; Meyers, R.A., Ed.; John Wiley and Sons: New York, 1998; pp 4797–4803.

Hurley, J.P.; Nowok, J.W.; Bieber, J.A.; Dockter, B.A. Strength Development at Low Temperatures in Coal Ash Deposits. *Prog. Energy Combust. Sci.* **1998**, 24, 513–521.

Mann, M.D. *Characterization of Fluid-Bed Combustion Deposits*; Final Report for Lockheed Martin Idaho Technologies Company; EERC Publication 98-EERC-03-01; Energy & Environmental Research Center: Grand Forks, ND, March 1998.

Pflughoef-Hassett, D.F. *Task 1.13 – Data Collection and Database Development for Clean Coal Technology By-Product Characteristics and Management Practices*; Final Topical Report (Jan 1, 1997–June 30, 1998) for U.S. Department of Energy Contract No. DE-FC21-93MC30097; EERC Publication 98-EERC-10-13; Energy & Environmental Research Center: Grand Forks, ND, Oct 1998.

1999

Dockter, B.A. Impact of Coal Fly Ash on Set Time of Concrete. Presented at the American Coal Ash Association 13th International Symposium on the Management and Use of Coal Combustion Products (CCPs), Orlando, FL, Jan 10–14, 1999.

Dockter B.A.; Eylands, K.E.; Hamre, L.L. Use of Bottom Ash and Fly Ash in Rammed-Earth Construction. In *Proceedings of the 1999 International Ash Utilization Symposium*; Lexington, KY, Oct 18–20, 1999.

Hassett, D.J. A Generic Leaching Procedure to Predict Environmental Impact of Reactive Materials Such as Coal Combustion By-Products. Presented at the 15th Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, July 18–21, 1999.

Hassett, D.J.; Daly, D.D.; Pflughoef-Hassett, D.F. Current Practices and Issues for Placement of Coal Combustion By-Products in Mine Settings. Presented at the Western Region Ash Group 2nd Annual Coal Combustion Products (CCPs) Forum – CCP Utilization in Mining Applications, Scottsdale, AZ, Aug 17, 1999.

Hassett, D.J.; Eylands, K.E. Mercury Capture on Coal Combustion Fly Ash. *Fuel* **1999**, 78, 243–248.

Hassett, D.J.; Mann, M.D.; Pflughoef-Hassett, D.F.; Henderson, A.K.; Eylands, K.E.; Ruckstuhl, K. Environmental Performance of CFBC By-Products. In *Proceedings of the 1999 International Ash Utilization Symposium*; Lexington, KY, Oct 18–20, 1999.

Hassett, D.J.; Mann, M.D.; Pflughoef-Hassett, D.F.; Henderson, A.K.; Ruckstuhl, K. Characterization of a Fluidized-Bed Combustion to Determine Potential for Environmental Impact. Presented at the American Coal Ash Association 13th International Symposium on the Management and Use of Coal Combustion Products (CCPs), Orlando, FL, Jan 10–14, 1999.

Hassett, D.J.; Pflughoef-Hassett, D.F.; Laudal, D.L.; Pavlish, J.H. Mercury Release from Coal Combustion By-Products to the Environment. In *Proceedings of the 1999 International Ash Utilization Symposium*; Lexington, KY, Oct 18–20, 1999.

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Pavlish, J.H. *Mercury Stability in the Environment*; Final Topical Report (April 15, 1998 – June 30, 1999) for U.S. Department of Energy Cooperative Agreement No. DE-FC26-98FT40320; EERC Publication 99-EERC-09-03; Energy & Environmental Research Center: Grand Forks, ND, Sept 1999.

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Dockter, B.A. *Freeze–Thaw Testing for City of Winnipeg Revised Pavement Mixes*; Final Report; EERC Publication 2000-EERC-10-03; Energy & Environmental Research Center: Grand Forks, ND, Oct 2000.

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Pflughoef-Hassett, D.F. Practical Working Definition for Materials from Conversion of Coal for Power Production. *Energeia* 2000, 11 (4).

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Pflughoef-Hassett, D.F.; Dockter, B.A.; Hassett, D.J.; Eylands, K.E.; Hamre, L.L. *Use of Bottom Ash and Fly Ash in Rammed-Earth Construction*; Final Report for North Dakota Industrial Commission Contract No. NDIC LMFS 99-29; EERC Publication No. 2000-EERC-09-03; Energy & Environmental Research Center: Grand Forks, ND, Sept 2000.

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5.0 CONCLUSIONS

Conclusions from individual CARRC tasks/activities were noted in the previous section describing the accomplishments of CARRC from 1998 through 2007. General conclusions drawn from the work performed and interaction with CARRC members, special project sponsors, and other CCB industry stakeholders are:

- Changes in fuels, operations, emission controls, and other generation-driven factors impact the quantity and character of CCBs in the United States, and research is needed to ensure that these materials are managed appropriately.
- Development of technically valid information on the characteristics and performance of CCBs facilitates appropriate management of CCBs, development of utilization practices and standards, development of beneficial use rules, and responses to regulatory questions.
- CARRC provides a communication network for members and special project sponsors and a communication conduit for information transfer to government agencies, industry groups, and other stakeholders.

6.0 REFERENCES

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