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March 29, 2017

Karlene Fine
Lignite Research Council
North Dakota Industrial Commission
State Capitol
600 East Boulevard Avenue
Dept. 405
Bismarck, ND 58505-0840

RE: Transmittal Letter for Lignite Research Council Funding Application of Expansion Energy LLC

Dear Ms. Fine,

Please accept the enclosed application package for funding support from he Lignite Research Council and the North Dakota Industrial Commission for Expansion Energy LLC's proposed Phase II Small Research Project for demonstrating the patented "VCCS$^{\text{TM}}$ Cycle" technology utilizing ash derived from ND lignite coal and flue gas from the combustion of lignite coal.

Expansion Energy acknowledges that this Transmittal Letter sets forth a binding commitment from Expansion Energy to complete the project as described in the application, if the North Dakota Industrial Commission approves the requested grant.

Sincerely,

David Vandor
Managing Director & Chief Technology Officer
Email: dvandor@expansion-energy.com
Tel.: 914 631 3197

Carbon Capture & Utilization Using "VCCS^{TM} Cycle" Technology – Phase II:

Mineralization of Acidic Flue Gas CO_2 via Chemical Reaction with Alkaline Lignite Fly Ash
+
Extraction of Marketable Minerals & Other Commodities from Lignite Fly Ash

Applicant:

Expansion Energy LLC
26 Leroy Avenue
Tarrytown, NY 10591

Principal Investigators:

David Vandor, Chief Technology Officer
Expansion Energy

Sandra Broekema, P.E., Manager of Business Development
Great River Energy

Bruce C. Folkedahl, Senior Engineer
Energy & Environmental Research Center

April 1, 2017

Amount Requested: $62,000

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Figures and Tables

Abstract

In 2016, Expansion Energy LLC ("XE"), with participation and support from Great River Energy ("GRE"), successfully completed a Phase I project to design and estimate the capital costs for a modular pilot plant ("Pilot Plant") utilizing XE's patented "VCCS^{TM} Cycle" carbon capture & utilization technology. VCCS neutralizes CO_2 from power plant flue gas by chemically reacting it, in the presence of methanol, with alkaline lignite coal ash, yielding marketable solid mineral materials, including high-value rare earth elements ("REEs") and other metals.

Building on the results achieved in the Phase I work, XE and GRE, with the participation of the Energy & Environmental Research Center ("EERC"), proposes a Phase II project ("Project") to demonstrate at a laboratory scale the carbonization chemistry of VCCS and to establish the extent to which REEs and other valuable compounds can be derived from VCCS.

In a subsequent Phase III project, XE, GRE and other qualified entities would partner to deploy the Pilot Plant designed in Phase I for field demonstrations using flue gas CO_2 and lignite coal ash from GRE's lignite-fired Spiritwood power plant in ND.

Successful Phase I, II and III projects would significantly enhance the value of lignite coal and the beneficial use of lignite ash by providing additional revenue streams from marketable lignite-derived commodities and by reducing CO_2 emissions from ND's lignite-fired power plants without relying on CO_2 emissions regulations.

In addition to advancing the VCCS Cycle's Technology Readiness Level ("TRL") for eventual commercial deployments, specific objectives and deliverables of the Phase II project will include the following:

- Establish the extent to which alkaline coal ash can be neutralized by acidic flue gas, combining CO_2 in the flue gas and (for example) CaO in the fly ash into calcium carbonate;
- Establish the extent to which a select group of high value REEs and other metals now concentrated in the coal ash will be leached into a wet methanol stream that is a byproduct of the carbonization process, allowing that wet methanol with its concentrated REEs and other metals to be further processed as a source of high-grade REEs;

- Establish the extent to which the carbonates found in the VCCS-treated ash can be distinguished and separated from the other solids, allowing those solids to be further treated for REE and other metal separation.

This Phase II Project will result in the laboratory-scale demonstration (by EERC) of the carbonization aspects of VCCS (using actual flue gas from EERC's testing facilities and fly ash derived from lignite and supplied by GRE), and the analysis of the REE content of the wet methanol that hosts the carbonization reaction. The laboratory testing will replicate the ChemCad process designed and analyzed in the Phase I Project, which was developed by XE and R.C. Costello Associates, and which was based on XE's patented VCCS Cycle. In addition to the two tasks outlined above, EERC will characterize the treated (neutralized) ash material regarding the potential for physical separation of such distinct components as sand, carbonates, and the like. The characterization of the treated ash may include the distinctions between the various treated-ash components based on size (grain) and on mass, allowing the Project team to make preliminary conclusions regarding the extent to which any portions of the treated ash might be physically/mechanically separated from other portions.

The duration of this Project is 2-3 months, including the reporting period.

Total estimated Project costs are **$124,000**, of which XE will provide **$37,000** (29.8%) and Great River Energy will provide **$25,000** (20.2%), covering 50% of the total Project costs.

Project Summary

XE, with participation and support of GRE and EERC, proposes a Phase II Project to confirm the carbonization (ash neutralization and CO_2 uptake) potential of VCCS, establish the extent to which REEs and other valuable metals leach into the wet methanol that is continuously withdrawn from the VCCS reaction vessel, and establish the extent to which the carbonates that are formed in the neutralized dry products of VCCS can be separated (in subsequent experiments), allowing the remaining solids to be further treated (chemically and mechanically) for REE recovery.

The attached EERC proposed work program includes the following tasks:

- **Task 1,** Flue Gas Interaction Test: EERC's small-scale pressurized fluidized-bed combustor (PFBC) will provide flue gas to the testing protocols, which will closely replicate the flue gas conditions at GRE's lignite-fired power plants and other ND lignite-fired plants. That flue gas will be introduced to a slurry of ash and methanol, where the ash is from one of GRE's coal-fired power plants. Several samples with various degrees of moisture content will be tested.

- **Task 2,** REE Analysis: The analysis of REE "leaching" from the ash to the wet methanol will establish the extent to which 7 specific elements leave the ash and exit in the withdrawn wet methanol, or remain with the solids. In this task, the solids will be analyzed for REE content.
- **Task 3,** Carbonate Analysis: In this task, decanted wet methanol will be analyzed for REE and other metals content. Also, the treated ash solids will be analyzed for carbonate "characteristics", such as the size distribution of the carbonates, allowing the team to make projections about the potential for mechanically removing the carbonates from the treated ash, thus allowing further treatment of that ash for additional REE and other metals separation.

The following seven (7) elements will be tested as "proxies" for approximately 24 valuable REEs and other metals that are found in lignite ash: Cobalt, Gallium, Germanium, Holmium, Scandium, and Thulium. Limiting the testing to those elements allows for "budget control" without sacrificing the Project team's ability to make projections about the recovery potential of the other REEs and other metals in lignite ash.

In a subsequent Phase III project, XE and Great River Energy would partner (likely with others) to deploy the Pilot Plant designed in Phase I for field demonstrations using flue gas CO_2 and lignite coal ash from Great River Energy's lignite-fired Spiritwood power plant in ND.

Successful Phase I, II & III projects would significantly enhance the value of lignite coal and lignite coal ash by providing additional revenue streams from marketable lignite-derived commodities and by reducing CO_2 emissions from ND's lignite-fired power plants without relying on CO_2 emissions regulations.

A main general objective of the Project is to advance the VCCS Cycle's Technology Readiness Level ("TRL") for subsequent demonstration-scale and eventual commercial-scale deployments.

Specific deliverables of the Phase II project will include:

- EERC's report of its findings regarding the three tasks outlined above and in the attached proposal by EERC.

- XE’s report (with GRE input) as to the technical and economic significance of EERC’s findings.

This Phase II Project will result in a deeper understanding of the many values offered by VCCS, which should enhance the value proposition for advancing the Phase III Pilot Plant.

Project Description

VCCS Cycle Technology Overview

XE’s patented “VCCS^{TM} Cycle” carbon capture & utilization technology neutralizes CO_2 (an acid on the pH scale) by reacting it with alkaline coal ash in a series of classic acid + base reactions, yielding precipitated, stable, solid carbonate mineral material (i.e., “mineralization”) in a manner that requires very little additional energy input. The VCCS Cycle is a scalable, continuous process, where CO_2 binding reactions occur on a short timescale (measured in seconds), making the VCCS Cycle suitable for large-scale lignite-fired power plants. VCCS uses primarily basic process equipment which is in abundant supply at low capital cost and does not require long lead times, such as reaction vessels, blending equipment and augers, basic PLCs, standard piping, etc.

VCCS uses processes and inputs that achieve marketable final products, which are dry, easy to handle, store and transport. The byproducts of VCCS (including REEs and other metals) can generate substantial revenues to support the deployment of VCCS plants adjacent to coal-fired power plants or coal ash pits.

VCCS provides multiple solutions for the challenges and opportunities related to lignite-fired power generation, including:

1. **Capturing and permanently sequestering a portion of the CO_2 emitted from lignite-fired power plants**, without having to sequester CO_2 underground and without involving expensive CO_2 pipelines and compressors, which are required by other carbon capture & sequestration systems. Instead, VCCS’s outputs are marketable solids that require no pipelines or underground sequestration.
2. **Treatment and beneficial use of coal ash** produced at lignite-fired power plants to the point that the ash’s valuable and/or potentially harmful components can be separated out, leaving an environmentally benign residual material that can be further refined and marketed or safely landfilled.

3. “**Harvesting” valuable minerals** (such as rare earth elements, uranium, germanium, aluminum, nickel, iron oxide, etc.) **and other materials from coal ash**, which can generate substantial revenues via sale of those commodities to the market.

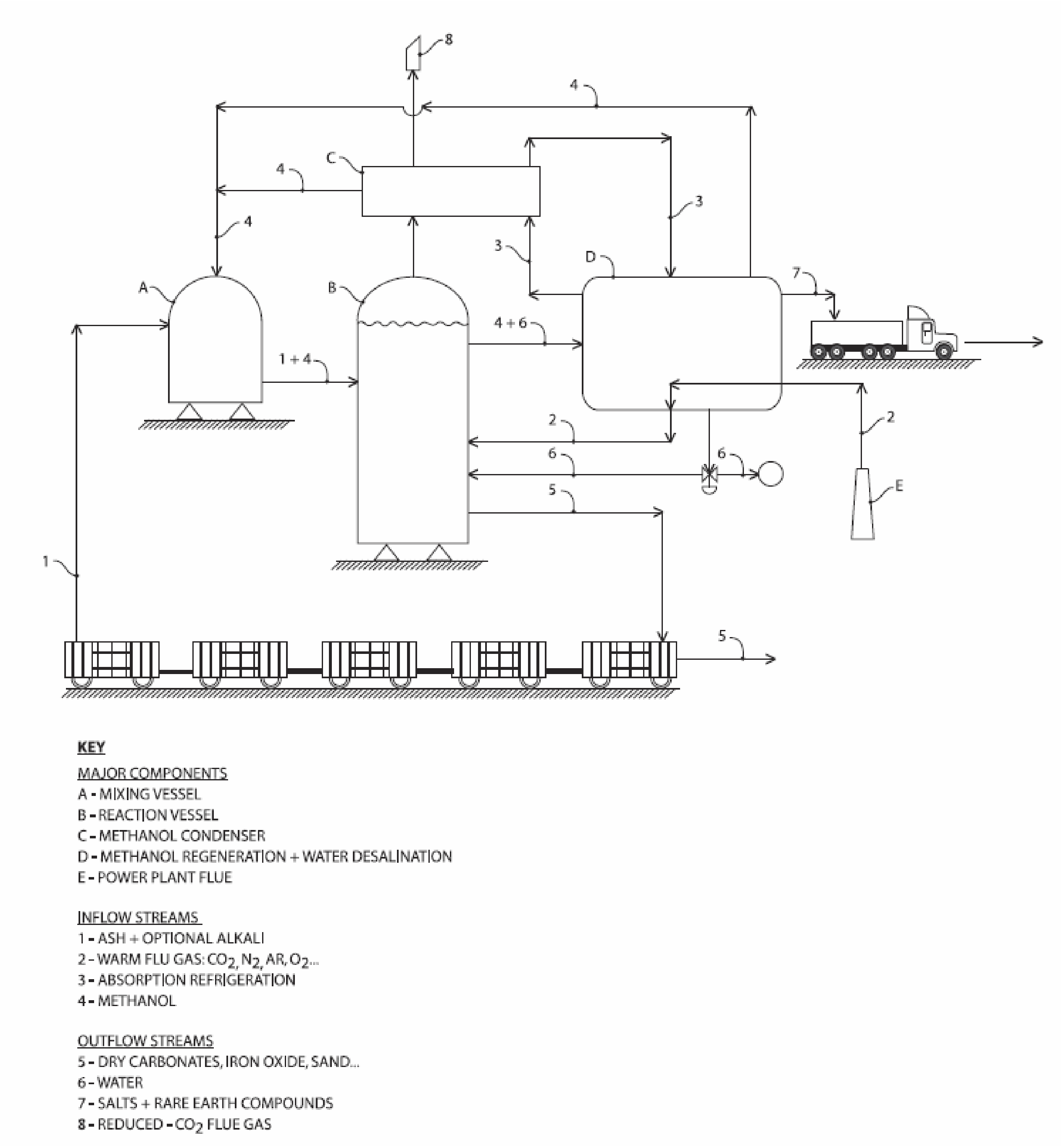
4. **Producing safe (treated) bulk materials for numerous industrial and construction applications.** Bulk byproducts, such as calcium carbonate, derived from the VCCS Cycle can be utilized as agricultural inputs (i.e., fertilizer); as a limestone substitute; for construction materials; for the treatment of contaminated soils; and for numerous other commercial applications.

5. **Augmenting (or eliminating the need for) electrostatic precipitators at coal-fired power plants** by inherently removing particulate ash matter from flue gas as that flue gas moves through the VCCS system. This would reduce capital costs, parasitic power losses and operating costs related to electrostatic precipitators deployed at coal-fired power plants today.

6. **Augmenting (or eliminating the need for) SO_2 removal systems at coal-fired power plants** by chemically reacting the acidic SO_2 with alkaline coal ash to neutralize SO_2 in substantially the same way that VCCS neutralizes CO_2. This would reduce capital costs, parasitic power losses and operating costs related to SO_2 removal systems deployed at coal-fired power plants today.

Thus, the VCCS Cycle technology has the potential to achieve carbon capture & utilization in a profitable, sustainable manner that does not rely on regulatory or legislative CO_2 reduction mandates for its economic viability.

Figure 1: VCCS Cycle – Process Schematic



The VCCS reactions are hosted in a non-aqueous solvent, methanol, allowing the carbonates to precipitate out of the reaction without carrying water. **Key steps of the VCCS Cycle process** are as follows, referencing Figure 1 above:

1. Methanol is blended with the alkaline coal ash in a mixing vessel (A), producing a methoxide solution, and sent to a reaction vessel (B). Using methanol allows the carbonates to precipitate out of the reaction without carrying water. That innovation avoids a water-laden product stream and eliminates the need for energy-intensive separation of "salts" from saltwater.
2. The CO_2-carrying flue gas (and some moisture) from (E) is bubbled through the methoxide in reaction vessel (B), allowing for the acid + base reaction. Specifically, the acid CO_2 contained in the power plant's flue gas reacts with the alkaline calcium oxide and other basic metal ions in the coal ash, resulting in inert materials such as calcium carbonate (limestone), iron oxide and sand.
3. The wet (aqueous) methanol is continuously regenerated in (D), such that the water content in the reaction vessel is under certain limits. VCCS also includes a novel methanol regeneration step that uses refrigeration (but requires little external energy), which occurs in (D) before being sent back to (A) for further use. The recovered water from (D) can be used for power plant cooling or other industrial or agricultural purposes (after additional filtration).
4. The solid, dry carbonates that result from the acid + base reaction, plus the residual sand and iron oxide, are continuously removed from the reaction vessel (B), and are ready for use in the variety of industrial, construction and agricultural applications. Similarly, the continuous methanol regeneration process yields a wet byproduct that is a concentrated liquid, which contains metal salts, including significant proportions of rare earth elements. That recovered "liquor," which can be further processed at an off-site metals recovery facility, can be a source for valuable rare earth elements, helping the United States avoid the need to import critical rare earth elements from China (where ~ 95% of the world's rare earth elements are produced today).

Phase II Project Objectives

Per the EERC proposed protocols (attached) the lab work and subsequent analysis will have three objectives:

1. Demonstrate the extent to which alkaline lignite ash can be neutralized by acidic flue gas (in the presence of methanol), converting metal oxides such as CaO into carbonates such as calcium carbonate.
2. Determine the extent to which the REE content of the ash leaches into the wet methanol that hosts the VCCS reaction, allowing a decanted stream of wet methanol to be a concentrated "carrier" of REEs
3. Determine the extent to which the solid carbonates that are mixed with the other treated solids can be distinguished from the sand, aluminum oxide (and other solids), so as to allow for the mechanical separation of the carbonates and thus allowing for further treatment of the neutralized ash solids, without risking the release of CO_2 from carbonate-containing solids.

Following the successful completion of Phase II, a subsequent Phase III project would build, deploy and test the Pilot Plant designed in Phase I of these studies.

Standards of Success

The standards of success for the Phase II Project include the following:

1. Confirm that the entire alkaline content of the sample lignite ash was converted to carbonates by the VCCS technology.
2. Remove wet methanol from the reaction vessel(s) and establish the extent to which the wet methanol contains some portion of the REEs and other metals that were in the pre-treated ash. Approximately 7 REEs and other metals will be measured.
3. Calculate the amount of REEs and other metals that remain in the treated ash, and characterize the grain sizes and molecular mass of the carbonates relative to the other components (such as sand) that constitute the bulk of the treated ash.

The knowledge gained from Phase I and from Phase II will inform a Phase III LRC funding submission for the construction, deployment and operation/demonstration of an appropriately scaled VCCS Pilot Plant at Great River Energy's Spiritwood power plant, which XE plans to submit in partnership with Great River Energy and possibly other qualified entities. If successful, Phase III would, in turn, inform the potential commercial deployment of one or more full-scale VCCS Cycle plants at Spiritwood Station or at other ND lignite-fired power plants. The applicant understands that a positive decision by LRC to support this Phase II application does not guarantee that LRC will support the funding of Phase III.

Background

XE's objective in inventing and patenting the VCCS Cycle technology was to develop and eventually commercialize a carbon capture technology that can achieve meaningful reductions in CO_2 emissions from power plants (and other CO_2 emission sources) through processes that also provide substantial ancillary revenue streams, making these systems less reliant on public policies & regulations to achieve economic sustainability and widespread deployment. A related objective is to beneficially utilize and simultaneously remediate the abundant supplies of coal ash which exist in North Dakota and around the world, and to achieve greater economic value for this byproduct material by extracting valuable minerals and bulk commodity materials that can be sold to separate markets.

Under the direction of XE, laboratory testing of the VCCS Cycle using ND lignite coal ash has been previously performed by Wyoming Analytical Labs and analyzed by an independent chemical engineering consultancy: Thomas Schuster Consultants. This lab-scale work has validated the overall technical viability and efficacy of the Cycle, and provided important findings related to material balance and energy balance which will be instructive for the proposed Phase II Project. These tests and analyses have also confirmed that methanol is a superior "host" material for the CO_2 + alkaline chemical reaction. Utilizing methanol as the host material yields a dry, powdery (i.e., flowable and non-sticky) slate of resulting products (carbonates, iron oxide, sand, etc.), and the methanol is easily recovered for reuse in the Cycle. See the attached "VCCS Cycle Research Report."

In addition, that lab-scale work showed methanol to be an effective solvent for extracting a range of valuable minerals from lignite coal ash, thereby making such separated minerals marketable, and substantially reducing (or virtually eliminating) the heavy metals load of the carbonates and other byproducts produced by VCCS.

XE's completed lab-scale work is a strong foundation for further commercialization of the VCCS technology, beginning with the Phase I Project previously completed and continuing with the Phase II Project proposed herein, and advancing further thereafter with the Phase III Pilot Plant field demonstration.

Qualifications

In addition to the qualification summaries below, please see the attached bios of Key Personnel for the Project.

Company Qualifications

Expansion Energy LLC (Tarrytown, NY; www.expansion-energy.com) is a developer and licensor of breakthrough technologies (including the VCCS Cycle) related to the production, transport, storage and conversion of energy, as well as industrial-scale energy efficiency. XE's business model is largely to license its proprietary technologies to other companies, including end users in the energy industry as well as global energy equipment OEMs.

XE currently holds more than 30 granted US and global patents, with numerous additional patent applications currently being reviewed by various patent authorities globally. Most of XE's technologies rely on its deep expertise in the disciplines of gas processing, industrial process design, and cryogenics.

XE has successfully commercialized a portion of its technology portfolio, in partnership with corporate licensees of our technology, and is continuously commercializing its newer technologies, as they achieve patented or patent-pending status.

In addition to many projects for completed for private sector energy companies, XE has successfully completed multiple technical and economic studies for the New York State Energy Research & Development Authority (NYSERDA) related to the deployment of XE technologies in New York and related to third-party technologies and energy-related public policy. XE has also successfully completed projects for the California Energy Commission and the Gas Technology Institute.

Great River Energy (Maple Grove, MN; www.greatriverenergy.com) is one of the largest consumers of North Dakota lignite, operating several large lignite-fired power stations in ND. As such, GRE also has extensive experience with ash processing, disposal and beneficial use, as well as with flue gas emission control systems and processes. GRE is a national leader in energy innovation, and has successfully completed several prior studies for the Lignite Research Council in partnership with other ND lignite companies, including projects that have resulted in the full-scale commercialization of the technologies supported by LRC funding, such as the proprietary "DryFining" process.

University of North Dakota Energy & Environmental Research Center (EERC; Grand Forks, ND; www.undeerc.org). The EERC is recognized as one of the world's leading developers and evaluators of cleaner, more efficient energy and environmental technologies. The EERC conducts research, development, demonstration, and commercialization activities; and is dedicated to moving promising technologies out of the laboratory and into the commercial marketplace. In partnership with private industries, government agencies, and academic institutions, the EERC conducts basic applied research and development of practical, problem-solving technologies and processes using the best combination of leadership, talent, equipment, and laboratory space available. The ultimate goal is to work in partnership with clients to develop, refine, demonstrate, and commercialize marketable products that provide practical solutions to real-world challenges.

Through the EERC's Coal Ash Research Center, the EERC is leading the nation in the utilization and disposal of coal by-products. Among numerous other areas of expertise, the EERC has been involved in research and development of clean coal technologies for over 50 years and is the world's leading research and development center for coal, with special emphasis on low-rank coal such as lignite. EERC research, development, demonstration, and commercialization programs are designed to embrace all aspects of energy-from-coal technologies from cradle to grave, beginning with fundamental resource characterization and ending with waste utilization or disposal in mined land reclamation settings. Since its founding in 1951, the EERC has conducted research, testing, and evaluation of fuels, combustion and gasification technologies, emission control technologies, ash use and disposal, analytical methods, groundwater impacts, cofiring technologies, and advanced environmental control systems. The EERC team has more than six decades of applied research, development, and demonstration experience producing energy from all ranks of coal.

Key Project Personnel & Qualifications

The following will be the Key Personnel for the Project, including its Principal Investigators. Bios and qualifications for key team members are attached.

- David Vandor, Chief Technology Officer and Inventor of the VCCS Cycle, Expansion Energy
- Sandra Broekema, P.E., Manager of Business Development, Great River Energy
- Charles W. Bullinger, Senior Principal Engineer, Great River Energy
- Bruce C. Folkedahl, Senior Engineer, Energy & Environmental Research Center

Value to North Dakota

XE, with participation and support from Great River Energy, proposes to increase the total value of and demand for North Dakota lignite, and to contribute to the growth and longevity of North Dakota's lignite and lignite-fired power industries. In particular, successful commercial deployments of the VCCS Cycle technology (supported by the Phase I and Phase II projects discussed herein) could help extend the life of North Dakota's lignite-fired power stations by creating new "values" related to CO_2 emission reduction, ash neutralization, and the recovery of REEs and other minerals. Those new value streams will help preserve the jobs and economic activity in North Dakota (particularly in ND's lignite-producing counties) which are directly and indirectly related to the use of lignite for power generation.

If successfully deployed, the VCCS technology could provide multiple solutions for the challenges and opportunities related to lignite-fired power generation in North Dakota, including:

- Capturing and permanently sequestering a substantial portion of CO_2 emitted from lignite-fired power plants
- Treating coal ash produced at lignite-fired power plants so it can be utilized for numerous additional "beneficial use" applications.
- "Harvesting" valuable marketable minerals and other materials from lignite ash.
- Producing safe (treated) bulk materials for numerous industrial and construction applications.
- Augmenting (or eliminating the need for) electrostatic precipitators at coal-fired power plants.
- Augmenting (or eliminating the need for) SO_2 removal systems at coal-fired power plants.

Thus, the VCCS Cycle technology has the potential to achieve carbon capture & utilization in a profitable, sustainable manner that does not rely on regulatory or legislative CO_2 reduction mandates for its economic viability.

If the proposed Phase II (and subsequent Phase III) Project is successful, it could lead to the commercial deployment of the VCCS Cycle technology at one or more lignite-fired power plants in North Dakota, generating meaningful ancillary "beneficial use" revenue streams from the production/extraction of high-value metals and other commodity materials from lignite coal ash streams.

Such commercial VCCS deployments could eventually create dozens or hundreds of additional, well-paying, stable jobs for North Dakotans and substantial increases in general economic activity in North Dakota, particularly in ND's coal-producing counties. New jobs would be for employment at the VCCS plant(s) itself; jobs related to the transportation and storage of the commodity materials produced; and potential new value-added manufacturing of construction materials, fertilizer materials, and other products produced from the commodity materials coming from the VCCS plant(s). A significant number of additional nearby indirect jobs would also be expected from the deployment of a VCCS plant(s).

The proposed Phase II work will augment the previously completed Phase I work by quantifying the carbonization (ash neutralization) effect of VCCS, and the REE separation potential of the cycle. With those results in hand, the advancement of the Phase III Pilot Plant will become more feasible because, as a result of the Phase II work, the economics of VCCS will be more evident.

Management

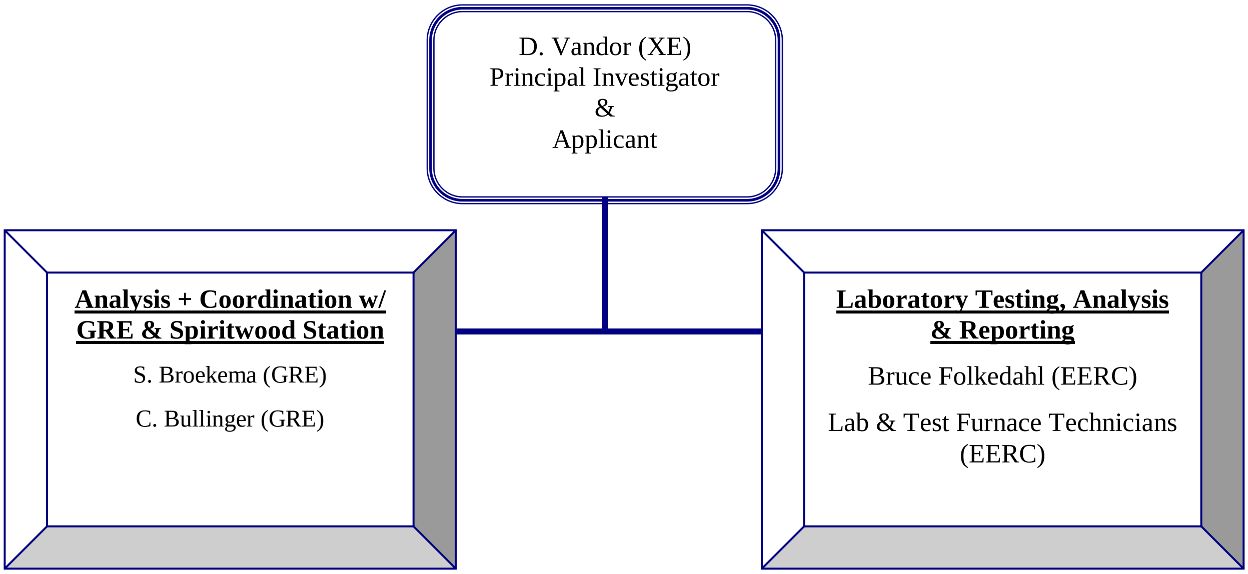
The proposed Project will be co-managed and coordinated by Mr. David Vandor (XE) and Ms. Sandra Broekema (GRE). XE will act as the primary applicant and contract coordinator. Vandor will serve as the contact point for the LRC & ND Industrial Commission, and will also coordinate technical matters with EERC.

Broekema will coordinate managerial, technical and logistical matters related to GRE and its Spiritwood Station, including the involvement of GRE Senior Principal Engineer, Charlie Bullinger.

EERC will complete the lab-scale VCCS work and the analysis of the liquid and solid streams that are derived.

The following organizational chart summarizes the management structure that will be used for the Project:

Figure 2: Project Management



The team identified in the above organizational chart is composed of the Key Personnel listed in the "Qualifications" section of this application. The Project team will meet as needed, primarily via teleconferencing, and otherwise communicate on a regular basis to stay coordinated and keep everyone apprised of relevant progress and developments. These meetings and communications will serve as the basis for the interim reports to LRC. The Project's Final Report will be created as a joint effort of the Project team, but primarily led by XE.

Timetable

The following are the proposed milestones and dates for completing the Phase II Project:

Week 1: Arrange and complete “kick off” conference call with full Project team

Weeks 2-3: Transfer pertinent data from XE and GRE to EERC; supply lignite and ash samples to EERC

Weeks 4-9: EERC completes the testing protocols and issues status report to XE and GRE

Weeks 10-11: XE submits Interim report to LRC

Weeks 12-14: Upon LRC’s comments on the Interim Report, XE and GRE will complete a final report that includes LRC’s comments and a qualitative review of EERC’s technical findings, especially regarding the extent of carbonization of the fly ash and as to REE recovery potential

Week 15-16: XE and GRE draft and deliver Final Report to LRC

Budget

Figure 3 is a summary of the Project budget. The total budget for the Phase II Project is **$124,000**. This Project will not require any materials or construction, and therefore the Phase II budget comprises only professional labor costs, packing and shipping of ash, and the time value of EERC laboratory work and the specialized equipment used in that work. The cost of EERC's work program is **$62,000**, per the proposal attached to this submission. XE will contribute at least 185 hours of in-kind technical and administrative support at $200/hour, for a total value of at least **$37,000.** XE's in-kind support will include technical coordination with ERC regarding the testing protocols and the interpretation of results. XE will also review and report on the economics of REE recovery and processing, placing the EERC findings regarding REE recovery potential into a "cost-benefit" context. GRE will contribute at up to 100 hours of in-kind technical and administrative support as well as the collection, packing and shipping of ash samples for a total in-kind contribution of **$25,000**. Thus, of the total **$124,000** budget, we request **$62,000** (50%) from LRC.

Figure 3: Budget Summary

Description	Professional Labor
GRE Technical & Admin. & Ash	$25,000
XE Project Mgt., Technical & Admin.	$37,000
EERC Lab Work & Analysis	$62,000
Total Budget	**$124,000**
Total Budget Request from LRC	**$62,000**

This Project is a technology development project and, therefore, in itself has no immediate return on investment. However, this Project is being undertaken with the intention of demonstrating and subsequently commercializing the VCCS technology, which will significantly improve the value of North Dakota lignite by multiple means. Therefore, the payback for this Project will come from the eventual commercialization of this technology.

Matching Funds

As outlined above and summarized in the table below, XE has agreed to provide a total contribution of **$37,000** to the Phase II Project. Great River Energy has agreed to provide a total contribution of **$25,000** to the Phase II Project. We are requesting that the North Dakota Industrial Commission join us in supporting this Project by committing **$62,000** to this Project through the Lignite Research Council.

Contributor	Contribution Type	Contribution Amount	Contribution %
Expansion Energy	In-Kind Services	$37,000	29.8%
Great River Energy	In-Kind & Ash	$25,000	20.2%
NDIC/LRC	Cash Grant	$62,000	50%
TOTAL		**$124,000**	**100%**

This Project will provide valuable information and improve the prospects of commercializing the VCCS technology for enhancing the value and competitiveness of North Dakota lignite by accessing new revenues from ND lignite and lignite coal ash and by reducing ND lignite's "environmental footprint." This will help ensure ND lignite's continued use for affordably priced power, even under tighter environmental/emissions constraints. More specifically, the Project will provide valuable technical and economic insights for a Phase III VCCS Pilot Plant program, which will improve the prospects of commercializing a new carbon capture and ash mitigation/beneficial use technology that will enhance the value and competitiveness of ND lignite.

Tax Liability

XE does not have any outstanding tax liability owed to the State of North Dakota or any of its political subdivisions. See the attached Affidavit.

Attachments

EERC Proposal

Affidavit of No ND Tax Liabilities

GRE Letter of Support

Bios of D. Vandor, S. Broekema, B. C. Folkedahl

VCCS Cycle Technology Report

EERC
Energy & Environmental Research Center®
Putting Research into Practice

University of North Dakota
15 North 23rd Street, Stop 9018 • Grand Forks, ND 58202-9018 • P. 701.777.5000 • F. 701.777.5181
www.undeerc.org

March 22, 2017

Mr. David Vandor
Managing Director & Chief Technology Officer
Expansion Energy LLC
26 Leroy Avenue
Tarrytown, NY 10591

Dear Mr. Vandor:

Subject: EERC Proposal No. 2017-0113 Entitled "Combustion Testing of VCCS™ Carbon Capture and Rare-Earth Element Process"

Introduction

Great River Energy (GRE) is evaluating Expansion Energy's (XE) VCCS™ carbon capture technology for use at its Spiritwood Power Generation Station. GRE would like to work with the Energy & Environmental Research Center (EERC) in evaluating not only the potential of the technology to capture carbon from flue gas but also to determine the ability of the technology to extract rare-earth elements (REE) from coal combustion ash.

Goals and Objectives

The EERC proposes to conduct a test series to establish the potential of the VCCS carbon capture technology for carbon capture and REE extraction. The goal of the testing will be to verify results of lab-scale tests using actual flue gas generated by the combustion of GRE-supplied coal in the EERC's pressurized fluidized-bed reactor (PFBR). Test objectives will include the following:

1. Submit fuel sample for analysis to determine its proximate, ultimate, heating value, bulk inorganic content, and ash sample for REE and other high-value metals (HVM) content.

2. Size fuel and bed material for combustion testing to match PFBR system requirements.

3. Perform combustion test under conditions similar to Spiritwood system conditions and bubble produced flue gas through a slurry of methanol and coal combustion ash from Spiritwood.

4. Collect test samples and analyze for bulk inorganic content and other HVM content, as well as CO_2 loading in the ash.

Description of Test Furnace

A pressurized fluidized-bed combustor (PFBC) has been constructed at the EERC to simulate the bed chemistry, ash interactions, and emissions from a PFB under closely controlled conditions. While the system was designed to operate under pressure, it is also capable of running under atmospheric conditions. A schematic of the PFBR is shown in Figure 1. This combustor is used for sorbent characterization, gaseous emissions including trace elements, agglomeration, and hot-gas cleanup testing in a cost-effective manner over a wide range of operational conditions. The 55-in.-tall reactor is constructed of 3-in. Schedule 80 pipe and is externally heated with three ceramic heaters. A hot cyclone

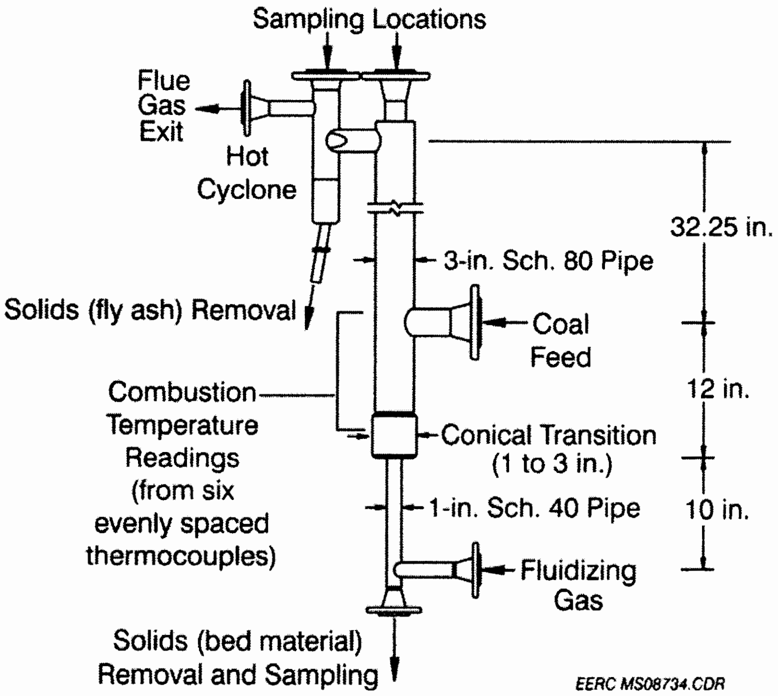


Figure 1. PFBC.

collects the ash and bed material that is carried out of the reactor. The preheated fluidizing gas can be a mixture of air and nitrogen or just air; in addition, one additional gas such as carbon dioxide, carbon monoxide, sulfur dioxide, or a nitrogen oxide can be added to result in a fuel gas similar to that generated in a full-scale FBC. Preheated gas at temperatures of up to 1400°F and pressures of up to 200 psig are supplied at the bottom of the reactor through a 1-in. Schedule 40 pipe. The fluidizing gas is supplied at sufficiently high velocities to prevent the sized bed material from dropping out during operation.

The fluidizing gas enters the 3-in. Schedule 80 main section of the reactor through a conical transition. This conical section was designed without a distributor plate to allow quick removal and quench of the bed material after completion of a test. Bed material can be sampled or collected using a lock hopper system located at the bottom of the combustor. Temperatures in the system are measured with 12 Type K thermocouples. These are located at 0.25, 1.75, 3.5, 5, 9, 11, 15, 23, and 43.25 inches above the conical transition section. Thermocouples are also located at the gas inlet, the cyclone exit, and the pressure letdown valve inlet. A sampling port is located downstream of the cyclone.

The use of electric heaters provides the capability to match the fuel feed rate to the amount of bed material in the reactor. External heaters are used for heating and maintaining the combustor and hot cyclone at temperatures of up to 1800°F for atmospheric operation and up to 1650°F for operation at 150 psig. The external ceramic heaters on the gas preheater are rated at 10.8 kW. The heaters on the combustor itself are divided into three zones: Zone 1 (at the bottom) is rated at 2483 W; Zone 2 (middle zone) is rated at 3650 W; and Zone 3 (upper combustor and cyclone) is rated at 3892 W. In a full-scale system, the bed is deep relative to that in the PFBC. Therefore, to keep the coal feed rate-to-bed inventory similar between bench- and full-scale systems, the coal feed rate in the PFBC is kept low relative to full-scale systems, compared on a fuel feed rate per bed cross-sectional area basis. Therefore, additional heat is required to maintain the desired temperature. The high heat losses through the combustor walls inherent to small-scale systems also require either good insulation or external heating. This type of heating system provides very good control of the reactor temperature.

Dry fuel and sorbent can be premixed at the desired ratio if required and then metered with a variable-speed auger into a common water-cooled auger, which in turn carries the material into the combustor. Two identical fuel hoppers ensure that fuel feed is not interrupted during hopper refills. A bed material hopper empties directly into the common auger, without flow control. Each hopper is maintained at a pressure slightly higher than that in the combustor during operation. The hoppers can be isolated from the system so that they can be refilled during a test. At the bottom of each hopper is a plastic sight tube; in addition, the fuel hoppers are equipped with sensors to alert the operator when the hoppers are empty and need to be refilled. A data acquisition and control system is used to monitor and record all critical pressures, temperatures, flow rates, and emissions. These critical data include the gas flow rates, bed static pressure and differential pressures across the bed and cyclone, and eight different internal combustor temperatures. The air and nitrogen flow rates are controlled automatically to flow rate set points. The combustor pressure is automatically controlled to a pressure set point. The three ceramic heaters on the reactor may be controlled manually to a given heater temperature or controlled automatically to maintain a desired gas temperature in each zone.

Work Scope

To accomplish the goals of the project, three tasks will be undertaken as follows.

Task 1. PFBR Flue Gas Ash Interaction Testing

The test conditions suggested for the PFBR testing include two flue gas moisture conditions to be utilized when introducing the flue gas to the slurry mixture of methanol and ash. Table 1 shows the test matrix for the PFBR tests. These two moisture levels are approximately 16% moisture and a midpoint moisture level between 5% and 10%.

The 16% moisture level will be attempted by no condensation of the flue gas with potential moisture input to the flue gas postcombustion, if needed, to reach 16% levels. The midrange will be produced by running a portion of the flue gas through a condensation system to remove all of the moisture from a portion of the flue gas and then recombining this dry flue gas with the remaining produced flue gas.

Table 1. Full Test Matrix

Test 1. 16% Moisture	Test 2. ~8% Moisture	Test 3. 16% Moisture/ No Sulfur
15-minute Flue Gas Contact	15-minute flue gas contact	15-minute flue gas contact
45-minute Flue Gas Contact	45-minute flue gas contact	

Combustion conditions for the PFBR will be matched as closely as possible to those conditions typical of Spiritwood which will be provided by GRE personnel. Conditions to be provided include bed throughput rate, coal feed rate, bed temperature, excess air, and sulfur retention in the bed. The EERC also requests that GRE provide the EERC with 50 lb of "seasoned" bed material from the Spiritwood plant to load the PFBR prior to beginning the test. This will eliminate the need for initiating the bed, reducing test period duration.

Coal and fly ash will also be provided by GRE for the testing. The EERC would like 200 lb of coal and 10 lb of fly ash from the Spiritwood Plant for this test series.

The ratio of the methanol to ash in the slurry will be at the same ratio as given in the mass flow specifications outlined in a previous communication between the EERC, GRE, and XE but at a reduced scale to match the flue gas flow rates of the PFBR. The slurry mixture will be placed in sealed containers with flue gas to be bubbled through the slurry mixture for 15 minutes at each of the three moisture conditions. The containers will be continuously stirred during the test period. Temperature and pH of the slurry mixtures will be measured at the start and end of each test period. An additional slurry mixture will be run in parallel under the same test conditions for a period of 45 minutes to determine if additional reaction time increases CO_2 uptake or REE extraction. At the completion of each test condition, the slurry samples will be collected and submitted to the laboratory for analysis.

Task 2. REE Analysis

The preparation for laboratory analysis will mirror that utilized in the previous consultant's lab-scale work. The methanol slurry samples will be filtered and both the filtrate and filter cake retained. The filter cake will be washed with methanol and the filtrate wash combined with the original filtrate. The filter cake will be dried and a portion submitted for thermogravimetric analysis (TGA) to determine CO_2 loading. All solid materials from the testing will be digested and analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) for REE and other HVM as requested by GRE and XE. Materials to be analyzed include the starting fly ash, postcombustion flue gas-contacted fly ash, and methanol filtrate. All samples will also be analyzed by x-ray fluorescence for bulk inorganic chemistry. The proposed list of REE and HVM analyzed for is presented in Table 2.

Task 3. Carbonate Analysis

Task 3 will consist of a test to determine the amount of material readily removed by magnetic separation and an analysis of the potential for separation of the carbonate fraction from the bulk of the ash. The magnetic separation test will consist of weighing an aliquot of fly ash, running the fly ash sample over a neodymium magnet, reweighing the fly ash sample to determine the amount of material removed, and then analyzing the removed material for chemistry. The magnetic separation tests will be performed several times to obtain a reasonable average for the fly ash sample. The carbonate separation analysis will be a computer-controlled scanning electron microscope (CCSEM) analysis of the fly ash sample after being exposed to the flue gas as a slurry in methanol. The methanol will be decanted off and the remaining ash sample analyzed by CCSEM. The CCSEM analysis provides a size distribution of the sample as well as a chemistry of each particle analyzed. This will identify if the carbonate particles are in a size range that can be readily removed from the ash by commercially available separation techniques, either by size or density fractionation. It is of value to be able to provide the carbonate material back to

Table 2. Elements of Interest
Cobalt
Gallium
Germanium
Holmium
Scandium
Thulium

the power plant, as this is a material the plant purchases regularly. This also allows the remaining ash to be further processed for other uses.

Budget

The estimated project cost for this proposed work is $62,000, with advanced payment of $20,000 prior to initiating work, $20,000 mid-point, and the remaining balance due at the end of the project. Initiation of the proposed work is contingent upon the execution of a mutually negotiated agreement between our organizations. The primary deliverable for the project will be the final project report, which will be completed within 5 weeks from the date of the test. This will provide ample time to collect and analyze test samples and prepare the final report. The data collected will be presented in tables and graphs, as deemed appropriate, with a discussion of the test results.

If you have any questions regarding the proposed work scope or schedule, please contact me by phone at (701) 777-5243, by fax at (701) 777-5181, or by e-mail at bfolkedahl@undeerc.org.

Sincerely,

Bruce C. Folkedahl
Senior Engineer

Approved by:

Thomas A. Erickson, CEO
Energy & Environmental Research Center

BCF/kal

EXPANSION
ENERGY

www.expansion-energy.com

March 20, 2017

Attn: Karlene Fine
Lignite Research Council
North Dakota Industrial Commission
State Capitol
600 East Boulevard Ave., Dept. 405
Bismarck, ND 58505-0840

Affidavit of No North Dakota Tax Liabilities

Through my signature below, I, David Vandor, Chief Technology Officer and Managing Director of Expansion Energy LLC with offices at 26 Leroy Avenue, Tarrytown, NY 10591, attest and confirm that Expansion Energy LLC has no outstanding tax liability with the State of North Dakota or any of its political subdivisions.

David Vandor

3/20/17
Date

GREAT
RIVER
ENERGY™

12300 Elm Creek Boulevard
Maple Grove, Minnesota 55369-4718
763-445-5000
greatriverenergy.com

March 22, 2017

Lignite Energy Council
1016 E. Owens Avenue
Bismarck, ND 58502

RE: Letter of Support for Phase II Lab Scale Verification - Expansion Energy VCCS^{TM} Cycle Process

Great River Energy believes that carbon capture and utilization may provide a pathway to maintaining and extending the viability of our base load lignite fired generating units in North Dakota under the future environmental regulations.

Prior research has indicated that carbon capture and sequestration is too energy intensive and costly to be practical anytime soon. Expansion Energy's "VCCS^{TM} Cycle" has some interesting characteristics that may make it much less energy intensive and potentially more cost effective with concentration of certain Rare Earth Elements.

Great River Energy has agreed to collaborate with Expansion Energy and EERC to verify the VCCS process under laboratory conditions more closely approximating actual flue gas with actual fly ash samples from Spiritwood Station. Phase II will also include testing of methanol leachate and resulting calcium carbonate for the presence and concentration of certain Rare Earth Elements.

Great River Energy will offer in-kind services (including collection, supply and transportation of DryFine coal, seasoned bed material and fly ash) and up to 100 hours of technical support for Phase II, total value $25,000.

We believe that this project will benefit the lignite energy industry in North Dakota while contributing to Great River Energy's mission of providing our owner-members with affordable, reliable energy in harmony with a sustainable environment.

Sincerely,

GREAT RIVER ENERGY

Sandra Broekema, P.E.
Director, Corporate and Business Development
(763) 445-5304

Cc: Mark Fagan
John Weeda
Charlie Bullinger
David Vandor, Expansion Energy
Rick Lancaster
John Bauer

Executive Biography – David Vandor

David Vandor is the Co-Founder & Chief Technology Officer of Expansion Energy LLC, which develops and owns innovative, patented and patent-pending energy-related technologies. David is the inventor or co-inventor of each of Expansion Energy's technologies. His Bachelor of Science degree was obtained from the City College of New York (CUNY) in 1969, followed by a Bachelor of Architecture in 1970. Through 1985, he achieved positions of increasing responsibility at the New York City Planning Commission, dealing with public policy and environmental issues. That was followed by several years of consulting, including for entities seeking cost-effective solutions for deploying alternative fuel vehicles (AFVs). By the mid-1990's, David's work focused exclusively on energy-related matters, through which he developed extensive expertise in the science of cryogenics, which is at the core of many of Expansion Energy's innovative energy & environmental technologies. His work during this period has included the following:

- Co-wrote the New York State "Alternative Fuel Vehicle Act of 1997", establishing incentives for the production and deployment of AFVs in New York State.
- Through 1998, was a member of the New York State Energy Research and Development Authority's (NYSERDA) LNG Study Group.
- In 1999, completed a study for US DOE's Brookhaven National Lab regarding the technical and economic issues associated with producing Liquid Natural Gas (LNG) from Landfill Gas (LFG).
- In 2001, completed NYSERDA PON 559, which offered "An Innovative Liquid Natural Gas (LNG) Storage Model."
- In 2002, completed NYSERDA PON 519-99, which focused on off-pipeline uses of LNG for heating and refrigeration; and quantified the value of "cold recovery" where LNG is vaporized prior to its use as a fuel.
- Also in 2002, with NYSERDA and Praxair co-funding, co-wrote a "Technology Evaluation of Small-Scale LNG Plants."
- From 2002 through 2005, served as a consultant to NYSEG and KeySpan Energy (now National Grid), regarding protocols for LNG systems.
- Through 2006, was a member of NYSERDA's LNG Steering Committee, helping to frame policy for LNG production, storage, transport, and dispensing in New York State.
- Also in 2006, began work on the invention of a cost-effective Small-Scale LNG Production System, which became Expansion Energy's patented "VX Cycle" technology.
- From 2004 through 2006, David completed "The Storage of Cold Compressed Natural Gas (CCNG) in Solution-Mined Salt Caverns," an in-depth R&D study which was co-funded by NYSERDA. The team included Geocomp, a world-renowned geotechnical consulting firm, which confirmed David's hypothesis that solution-mined salt caverns can be used to store cryogenic natural gas.

- Project Director for NYSERDA Contract #18814, examining the feasibility of deploying Expansion Energy's patented utility-scale power storage system, called the "VPS Cycle" at a steam-generating facility operated by Con Edison in New York City. The project team also includes equipment suppliers such as Dresser-Rand, Cameron and Chart Industries as contributors and peer reviewers.

David's R&D work focuses on developing innovative, patentable technologies that have demonstrable commercial value and address a known market need. The following is a sampling of Expansion Energy's patented technologies invented or co-invented by David Vandor:

U.S. Patent No. 7,464,557 B2, a "System and Method for Cold Recovery", granted on December 16, 2008. -- Cold Compressed Natural Gas (CCNG) is a supercritical phase of natural gas, achieved by moderate refrigeration (-116º F and colder), and moderate pressures (700 psig and greater), achieving approximately 85% of the density of LNG. The invention focuses on "cold recovery" during the "shift" from CCNG to CNG.

U.S. Patent 8,020,406, for a "Method and System for the Small-Scale Production of Liquid Natural Gas from Low-Pressure Pipeline Gas" (Granted in the U.S. and in Australia, and pending in other international jurisdictions.) A method and system (called the "VX Cycle") for the small-scale production of LNG using an innovative version of a methane expansion cycle, which does not require a high-pressure feed gas stream or a low-pressure outflow gas "sink". The VX Cycle uses natural gas as both the "product" and the "refrigerant".

U.S. Patent No. 7,821,158 B2, a "System and Method for Power Storage and Release", the "VPS Cycle", granted October 26, 2010. -- The VPS Cycle stores off-peak, low-value electricity as dense, liquid air (L-Air) in aboveground cryogenic vessels. The energy is released by pumping the L-Air to pressure, warming the now-compressed air by waste exhaust heat, and sending the hot, high-pressure air to the combustion chamber of a generator-loaded hot gas expander. During "send-out" the cold energy of the stored L-Air is recovered in a smaller "power loop(s)" that drives one or more additional generators.

U.S. Patent Application No. 12/247,902, for a "System and Method of Carbon Capture and Sequestration", the "VCCS Cycle". (Patented under "fast track" review by USPTO, per its Green Technology Pilot Program.) The VCCS Cycle captures CO2 in a non-aqueous solvent to which an alkali has been added. That alkali can include the alkaline ash (fly ash) that is produced at coal-fired power plants. The reaction between the acidic CO2 (as carbonic acid) and the alkali yields carbonates, water and heat. The non-aqueous solvent allows the carbonates to precipitate out of solution, yielding a dry powder that is non-toxic and has many post-production uses, while avoiding the need for energy intensive water removal (drying) of the carbonate. VCCS also provides for the recovery of valuable rare earth elements, other minerals, and bulk construction materials, while "detoxifying" the fly ash.

U.S. Patent 8,342,246, for "Fracturing Systems and Methods Utilizing Metacritical Phase Natural Gas" (Granted in the U.S. on 1/1/13, and pending internationally.) Vandor's Refrigerated Gas Extraction (VRGE) process uses locally available natural gas to fracture shales and tight hydrocarbon formations and to deliver the proppants used to allow the released hydrocarbons to flow to the surface. The core concept of VRGE is to use "like with like," i.e., to use natural gas (NG) to release and bring to the surface the hydrocarbons trapped in the formation, avoiding the use of large quantities of water "imported" to the well site and avoiding the need to bring costly fracturing fluids such as nitrogen, carbon dioxide or propane to the well site.

Sandra Broekema is currently Director of Corporate and Business Development for Great River Energy. She brings more than 20 years of experience in the energy industry focusing on R& D and new product commercialization in solar, wind and power generation. Sandra has a Bachelor's degree in Mechanical Engineering from the University of Minnesota - Institute of Technology and a Master's in Business Administration from the University of St. Thomas. She holds a Professional Engineering license in the State of Minnesota.

Sandra is responsible for Great River Energy's DryFining^{TM} commercialization program, working with clients to improve efficiency and reduce power plant emissions all over the world. She is also actively involved in recruiting additional steam partners for Spiritwood Station combined heat & power plant in North Dakota.

Great River Energy is a not-for-profit electric cooperative owned by 28 member distribution cooperatives. We generate and transmit electricity for members located across the state of Minnesota from the Arrowhead region in the northeast to the farming communities in the southwest.

Great River Energy owns and maintains a resource pool that includes 12 power plants and more than 4,600 miles of transmission lines. Great River Energy offers more than 3,500 MW of generation capacity from a diverse mix of coal, refused derived fuel, natural gas, fuel oil and wind.

Great River Energy is a Touchstone Energy® cooperative.

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Dr. Bruce C. Folkedahl is a Senior Engineer at the EERC, where he studies combustion and gasification for electricity generation; research on the fundamental mechanisms of ash deposition and fouling during the combustion process; process development for the conversion of fossil and biomass feedstocks to fuels, chemicals, and value-added products; and studies of corrosion and development of high-temperature materials to withstand aggressive combustion environments. Dr. Folkedahl has been responsible for the development of two novel technologies for water reduction in power generation systems. He received his Ph.D. degree in Materials Science and Engineering from Pennsylvania State University and his B.S. degree in Computer Science from UND.

Research Report

Chemical Analysis and Laboratory Testing of Expansion Energy LLC's

Patented "VCCS™ Cycle":

The Behavior of a Coal Fly Ash Sample Toward Carbon Dioxide Species In Methanol, Water, and Aqueous Methanol

Prepared by:

Thomas Schuster, Ph.D.

Thomas Schuster Consultants

Denison, IA

For:

David Vandor

Chief Technology Officer & Managing Director

Expansion Energy LLC

Tarrytown, NY

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Abstract

Chemical and process analysis was conducted to validate the core concepts of Expansion Energy LLC's patented "VCCS™ Cycle" technology for fly ash management/remediation and carbon capture and sequestration. Testing and analysis was designed to investigate VCCS's efficacy with respect to two key measures: (i) carbon dioxide binding; and (ii) the extraction (leaching) of representative trace materials from the fly ash.

A fly ash sample from a power plant utilizing lignite coal (North Dakota, USA) was investigated for carbon dioxide binding as well as the leaching of representative trace metals under three slurry carbonation conditions: (i) water; (ii) methanol (5% water); and (iii) "wet" (aqueous) methanol (~50% water). The resulting samples were analyzed by Thermogravimetric Analysis (TGA) for CO_2-loading and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for metals. The results indicate that:

(i) The fly ash sample was able to bind 0.28 tons of CO_2 per ton of fly ash;

(ii) Leachable metals were extracted during the slurry process

(iii) Carbonated fly ash samples derived from methanolic slurries have better handling characteristics than the samples originating from water slurries or aqueous methanol slurries

Notably, leaching and carbonation was accomplished on a 15-minute time scale, and the resultant carbonates were dry, powdery and easily handled (i.e., not "muddy") when derived from methanol slurries. These findings demonstrate the chemical and technical feasibility of the VCCS Cycle technology, and lay the foundation for further work. Future studies will focus on using other types of alkaline materials (instead of coal ash), metals leaching and metals recovery, to gain further insight into the design and economic parameters of the process. The extraction of hazardous and/or economically useful metals from the fly ash into the methanol solvent is an attractive feature that allows for the proper disposal of hazardous waste in concentrated form and/or for further processing to recover marketable elements/minerals—including valuable rare earth minerals plus "bulk" commodities for industrial, construction and agricultural applications.

Introduction

The generation of carbon dioxide (CO_2), fly ash and bottom ash from the combustion of coal and other fuels in thermal power plants presents significant environmental challenges. (Note: The term "fly ash" in this paper refers to both fly ash and bottom ash, including but not limited to coal ash.) Carbon dioxide is produced on a scale affecting global atmospheric chemistry and acidifying all major bodies of water, affecting aquatic species.

In addition, the fly ash that results from the combustion of coal represents a significant solid waste challenge, as experienced from the breaching of coal ash storage reservoirs at the Tennessee Valley Authority's Kingston Fossil power plant in December 2008. That breach caused acute environmental and health concerns, and will cost as much as $1.2 billion for clean-up and other liabilities.[1]

While fly ash can (for now) be utilized in road construction, cement manufacture and other building applications, much of it goes to landfills. Also, the waste lagoons (and dry piles) that store fly ash at its production source (e.g., at power plants) are sources of potential surface and groundwater contamination due to metals leaching out of storage, and from pH effects on the soil and groundwater.

As a result of the above factors, fly ash is facing the threat of increased regulation, including attempts to regulate this material as hazardous waste and to require more stringent methods for its disposal and treatment. Thus, there is a need for a cost-effective and ecologically and technologically feasible strategy to address the substantial volumes of fly ash generated by combusting coal (and other combustion fuels) and CO_2 emissions—and to economically extract the valuable materials contained in fly ash.

Carbonation of fly ash (such as occurs in the VCCS Cycle) has been correlated with reduced leaching of heavy metals and other salts from the ash into the environment, and often is referred to as "fly ash stabilization", with the product sometimes referred to as "stabilized fly ash".[2] The term "stabilization" or "stabilized" refers to the reduced hazard level of carbonated fly ash. In addition, fly ash loses a considerable amount of its fluidity when it is carbonated ('calcified') *in situ*. Predominant theories involve clogging of the microcrystalline pores, metal immobilization due to metal carbonate formation, and changes in the ash product pH profile.[3]

A main objective of Expansion Energy LLC's patented VCCS™ Cycle is to extract CO_2 from the effluent flue gas stream (e.g., from power plants) by reacting the acidic flue gas with the alkaline fly ash in the presence of a suitable (and novel) non-aqueous solvent, which results in the formation of an artificial limestone material—i.e., "mineralization"—thus reducing CO_2 emissions from power plants, incinerators and the like. The resulting materials are expected to find a variety of commercial uses while mitigating the hazardous and non-hazardous waste properties of the effluent gas and fly ash waste streams. In the VCCS Cycle, the fly ash is slurried in methanol and subsequently reacted with flue gas in a reaction vessel. Under these conditions, the CO_2 in the flue gas reacts with the calcium oxide (CaO) present in the fly ash to form calcium carbonate ($CaCO_3$). The essentially dry and flowable carbonated fly ash product resulting from the chemical reaction is separated, while the methanol is reused for further fly ash + CO_2 treatment. In applications at thermal power plants, the energy to drive the VCCS Cycle is derived from waste heat from the power station and supplementally from the heat generated by the chemical reaction itself.

The study described and discussed below represents the proof-of-concept for the VCCS Cycle, and is based on laboratory tests specifically designed to validate its chemistry. The stabilized fly ash product derived from the VCCS Cycle can be utilized in a variety of ways, such as:

- Fill material for road construction and building materials
- Agricultural inputs and artificial limestone
- Soil treatment / de-contamination
- Ocean de-acidification
- To extract rare earth minerals and other valuable materials (e.g., uranium, germanium, etc.)

Background

Coal predominantly consists of combustible organic matter with varying degrees of minerals dispersed throughout. The types and amount of these minerals depend on the grade of the coal and its geographic origin. The organic matter in coal is converted to CO_2 during the combustion process. The carbon dioxide-forming reaction of carbon with oxygen is the source of the heat that generates the steam for the production of electricity. Eq. 1 below shows the two elementary steps of the CO_2-forming process. Thermodynamically, most of the energy is freed in the first elementary step (Eq. 1a).

$$(1a)\ 2\,C + O_2 \longrightarrow 2\,CO$$

$$(1b)\ 2CO + O_2 \longrightarrow 2\,CO_2$$

It is during combustion that the minerals are concentrated in the fly ash product and some of the minerals are converted to their oxides. At this point, calcium oxide (CaO) becomes available and the sulfur and nitrogen oxides are formed as well. Nitrogen oxides are derived not only from the combustion of nitrogen-containing matter in the coal, but also by combustion of the nitrogen present in air. The primary sources of sulfur are the coal's organic components and, to a smaller extent, its mineral content. Mitigation of nitrogen oxide formation can be accomplished through the control of combustion conditions. Sulfur oxide production is determined by the coal itself as an intrinsic property, and it can be addressed by the application of sulfur "scrubbing" technologies.

The mineral composition of coal is caused by several factors. First, the mineral content roughly reflects the average abundance of the chemical elements in the earth's crust, which means that the likelihood of finding a certain element is proportional to its natural abundance in the earth's crust. Examples would be magnesium, titanium and aluminum. Since coal is derived from formerly living matter, certain elements are present above their natural abundance level in the earth's crust as they become enriched in plant or animal matter, such as calcium and sulfur. It is the presence of calcium, as CaO, that gives fly ash its potential for neutralizing CO_2 in flue gas. A third factor is the geochemistry of the region the coal originates from. Notable examples of this variation are the extent to which uranium and germanium are present. Uranium, in particular, is enriched in coal from phosphate bedrock, such as found in the Appalachian Mountains. The presence of uranium in fly ash, at quantities that add an extra degree of "hazard," also offers potential opportunities for uranium recovery. Metals recovery from fly ash will be the subject of a follow-up analysis in a subsequent paper.

For this report, Thomas Schuster Consultants (TSC) evaluated chemical data available in the public domain for North Dakota lignite coal, and the results are given in Appendix 1, which shows the average distribution of chemical elements in coal for the North Dakota coal basins. Data for 205 coal samples reported in the Coal Quality Database of the US Geological Survey was evaluated.[4] The largest variations for the predominant elemental species within the data base are for sulfur, silicon, iron and calcium, and the trace elements for barium.

The basic (alkaline) properties of fly ash are derived from the presence of alkaline metal oxides. Typically the primary alkaline is calcium oxide (CaO). Depending on coal composition, varying amounts of alkaline metal oxides such as sodium oxide (Na_2O), potassium oxide (KO), or barium oxide (BaO) contribute to the alkalinity of the fly ash. It is these alkaline metal oxides which give fly ash its carbonating properties, and thus its potential to capture and sequester CO_2. One key factor of carbonation is the aqueous chemistry of CO_2 (Eq. 2). Eq. 2 plus the additional equations that follow represent the carbonation portion of the VCCS Cycle.

Water sources for VCCS include the flue gas itself and the chemical reaction, so that water from external sources will not be required for VCCS. In fact, VCCS will produce water. VCCS requires that the ratio of liquid water to methanol in the reaction vessel be kept within certain limits.

$$(2)\ CO_2^{gas} \rightleftharpoons CO_2^{aq} + H_2O \rightleftharpoons HCO_3^{-} \rightleftharpoons H_2CO_3 \text{ or } CO_3^{2-}$$

The first step shown in (Eq. 2) is the physical dissolution of carbon dioxide gas by a given aqueous solvent system. This dissolution is reversible and the equilibrium is driven by the partial pressures of CO_2 in the gas and solvated forms. The bidirectional arrows indicate the reversibility of these processes. High partial pressures of gaseous CO_2 drive the dissolution and the equilibrium to the solution side (the left side). In general, the VCCS Cycle is enhanced by flue gas above atmospheric pressure.

The second step is the capture of the solvated CO_2 by water or a base to form carbonate in the free form (carbonic acid) or as an ion (carbonate itself). Ion formation depends on the alkalinity of the solution. The reaction is reversible as a whole, and the position of the equilibrium is governed by the alkalinity and acidity of the solvent and the partial pressure of gaseous CO_2.

Hydroxylic solvents—such as water or methanol—also play a role in making the alkaline oxides available for carbon capture. The fundamental reaction of water with CaO is given in (Eq. 3), and the equation for methanol (MeOH) given in (Eq. 4).

$$(3)\ CaO + H_2O \longrightarrow Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\,OH^{-}$$

$$(4)\ CaO + MeOH \longrightarrow Ca(OH)(OMe)$$

In methanolic solution, the following equilibria (Eqs. 5(a) and 5(b)) describe the principle behavior of the Ca^{2+}/CO_2 system after the initial solvolysis of the CaO.

$$\text{(5a)}\quad 2\,Ca(OH)(OMe) \rightleftharpoons 2\left\{Ca^{2+} + OH^{-} + OMe^{-}\right\} \rightleftharpoons Ca(OH)_2 + Ca(OMe)_2$$

$$\text{(5b)}\quad CO_2 + Ca(OR)_2 \rightleftharpoons (RO)CaCO_3R^1 \longrightarrow CaCO_3$$

$$R = H \text{ or } Me \qquad\qquad (\text{for } R = R^1 = H)$$

The choice of a solvent for the process is quite important. Water has a high boiling point and a significant latent heat of evaporation so it would be difficult to remove from a solidifying wet product and would result in a more cement-like, sticky product with poor handling properties. By contrast, a solvent like methanol (as used by the VCCS Cycle) is a better choice, since methanol is easier to remove and yields a dry, more powdery and easier-to-handle material.

The VCCS^{TM} Cycle

Expansion Energy LLC's patented VCCS^{TM} Cycle is illustrated by a Schematic Diagram (Appendix 2), which shows several major components of the continuous process. This section of the report offers a brief overview of the Cycle as illustrated by the Schematic Diagram.

The primary inflow streams to the Cycle are the alkaline ash stream from a coal-fired power plant, stream 1, (which may be augmented or replaced by alkalis from other sources), and the CO_2-containing flue gas, stream 2, produced by the power plant. Stream 1 is shown "arriving" by rail car because the original coal that produced the ash likely arrived by rail car, and any significant quantity of additional alkalis from off-site sources would also likely arrive by rail car. Stream 2 is shown to exit the power plant's flue (E) at some pressure and still warm, and possibly having been treated for contents other than its CO_2 content (e.g., SO_2, NO_2, etc.), but still containing trace amounts of moisture.

The ash stream (1) and any supplemental alkalis enter mixing vessel (A), which also receives pure methanol, as stream 4. Most of the methanol used in the Cycle is regenerated and sent back to the mixing vessel (A) for reuse as the primary solvent. However, some will be lost, requiring a make-up stream of methanol, which is not shown on the Schematic Diagram. Stream 1 becomes a suspension in stream 4, and is sent on to the reaction vessel (B) where the CO_2 contained in the flue gas from stream 2 (after having given up its heat content in subsystem (D)) reacts with the alkalis delivered by stream 1 + 4 to form carbonates, water and heat. Some components of stream 1 + 4, such as sand, remain unchanged and, along with the carbonates formed by the acid + base reaction, will precipitate to the bottom of the reaction vessel, to be mechanically removed as stream 5, returning to the railroad cars (or other means of transport) for delivery to off-site customers. Additionally a relatively small amount of water (6) derived from the methanol regeneration process may need to be added to the reaction vessel (B), augmenting the water produced by the acid + base reaction. However, the water content in the reaction vessel is strictly controlled, so that the methanol delivered by stream 1 + 4 is substantially the "host" solvent, offering a relatively "non-aqueous" medium in which the acid + base reaction occurs. That non-aqueous environment is the key to the "dry" precipitation of the sand, iron oxide and newly formed carbonates that leave the reaction vessel as stream 5.

In order to maintain the mostly non-aqueous conditions in the reaction vessel, wet (aqueous) methanol is removed from the top of the vessel as stream 4 + 6. That stream is sent on to subsystem D where the methanol, water and any salts carried by stream 4 + 6 are separated. (Less than 5% of the solids in the reaction vessel will travel with the 4 + 6 stream.) The regenerated methanol is returned to the mixing vessel as stream 4.

Those components of the flue gas (N_2, Ar, O_2) that do not react with the alkaline components of stream 1 will exit the reaction vessel as stream 8, and be vented or sent for further processing. To the extent that the alkaline content of stream 1 does not match the CO_2 flow rate in the flue gas (2), some CO_2 will also exit as part of stream 8. Up to 100% of the coal-fired power plant's daily ash stream can constitute stream 1, and up to 100% of the CO_2 content of the flue gas (2) produced daily can be neutralized, if enough alkali is added to stream 1.

The treated flue gas exiting the top of the reaction vessel (B) will carry some methanol vapor with it. That methanol is mostly recovered by condensation in a heat exchanger (condenser C), which is cooled by a flow of refrigerant. The condensed methanol (4) joins the larger regenerated methanol stream that arrives from subsystem D, with the combined methanol stream returned to the mixing vessel (A). The refrigeration (illustrated by stream 3) used in condenser C and in subsystem D is produced by absorption refrigeration (not shown), which is driven by several waste heat sources, including heat in the flue gas, heat produced during the mixing of the methanol with the alkalis in stream 1, and by the heat produced in the reaction vessel (B). That integration of the various heat sources and the absorption chiller is not shown on the Schematic Diagram.

The vast majority of the chemistry occurs in the reaction vessel (B), yielding almost as much solids in stream 5 (by weight) as entered the Cycle as stream 1. The function of subsystem D is to comprehensively treat the continuous but smaller wet methanol (plus salts) stream, separating it into regenerated methanol, water and solids (7) that are subsequently removed by truck (or other means of transport). This proprietary separation process yields separate liquid streams of methanol and water, and a separate stream of solids, stream 7, which will include various compounds (including those that contain valuable rare earth elements), which can be further processed for "byproduct" recovery and/or for treatment as toxic waste. In other words, unlike other CO_2 and fly ash treatments, the VCCS Cycle produces only a modest liquid waste stream, diverting some 95% of the solid products of the reaction vessel as a dry (non-aqueous) stream 5, and, significantly, the Cycle includes a viable deionization component suitable for cost-effectively treating the relatively modest liquid waste stream.

Study Design

The study was approached as a slurry process. The scale of a commercially deployed VCCS Cycle would accommodate the fly ash stream of a standard 500 MW coal fired power plant. A plant of that size produces approximately 400 to 450 tons of fly ash per day. Implementation of this process as a continuous flow process, as opposed to a batch process, would result in the turnover of roughly of 16 t/hr. of ash, which is a reasonable size for a single-reactor slurry process. This mass-over-time consideration determined the experimental time basis for the laboratory tests, which was set to the order of 10 to 20 minutes as an assumed residence time for ash in the reaction vessel.

The reaction conditions were chosen to show differences between water and methanol. In addition, carbonation experiments were conducted under two conditions. The first condition used aqueous sodium bicarbonate solution to simulate an indefinite CO_2 supply, and in the second set of experiments a simulated flue gas (80% nitrogen, 15% CO_2 and 5% O_2) was utilized to mimic power plant conditions. (The simulated flue gas condition is referred to throughout this report as the "purge gas" condition.)

It should be noted that the methanol used in this study was 95% methanol with 5% water. In the bicarbonate experiments, the final water content of the methanolic solutions was on the order of 50% due to the nature of the reagent. These high-water-content solutions are referred to as aqueous methanol in this report. The goal was to establish exhaustive carbonation data through the use of a carbonate reagent to serve as a reference point for the gas purge (simulated flue gas) experiments. Other data to be collected and reported were changes in the pH profile, weight and temperature changes. The temperature change data are necessary information for possible heat recovery opportunities from the reactor. The pH data might serve a possible basis for the development of process control strategies. An aliquot of the fly ash sample was separated crudely into ferromagnetic and non-ferromagnetic constituents. The idea was to see if trace metals and carbonation behavior move accordingly. The inclusion of indium in the determinations was based on its rareness and value, but also because of its routine use as an internal standard in ICP-MS. This use of indium often precludes its routine detection in samples unless unexpected results are investigated. The Test Plan submitted to the laboratory is reproduced in Appendix 3.

Laboratory

Laboratories for bidding were selected according to several criteria: technical capability, experience in the area of the study, reputation, and length of time in business. The study was granted to Wyoming Analytical Laboratories (WAL) based on those factors and pricing.

Discussion

Physical Descriptions

Sample

The fly ash sample was provided by Expansion Energy LLC, which is the developer and owner of the patented VCCS Cycle. The sample was a fine powder of blackish appearance. It was electrostatically charged, suggesting dryness. The sample was split by TSC into two samples in a 2:1 proportion. The lesser portion was magnetized and the magnetic particles crudely removed with a permanent needle magnet. The three resulting samples where submitted to WAL for laboratory testing and analysis. The sample with the original composition was labeled L8444, the magnetically enriched sample L8445, the magnetically depleted sample L8446.

Laboratory Observations

The laboratory communicated that the samples derived from highly aqueous solutions behaved poorly. They were difficult to filter, stuck to the laboratory equipment and were difficult to dry. By contrast, samples derived from methanol handled well, did not stick excessively to laboratory equipment and air-dried easily, yielding a manageable powder.

Instrumental Analysis

Carbon Load

The carbonated fly ash samples were submitted to TGA in order to establish the amount of carbon loading. The measurement principle is that the weight of a sample is monitored while it is heated and weight losses are noted. In this case, weight loss in temperature ranges above 450° C is attributed to the thermal loss of CO_2. Figures 1 and 2 at the end of this paper give example TGA curves in Time (s) *vs.* Loss representation. The loss of CO_2 is well defined in the data and starts at approximately 1500 s (450° C). The curves return to baseline after the transition, indicating completeness of decarboxylation. Tables 1 through 3 summarize the results of the analyses and predictions.

Table 1: Carbon Dioxide loading in Weight Percent.

Sample	Water (Gas Purge)	Water (Bicarbonate)	Methanol (Gas Purge)	Methanol (Bicarbonate)
Bulk Fly Ash	28.37	33.63	28.52	31.85
Magnetic Component	25.64	29.26	22.06	27.33
Non-Magnetic Component	27.19	33.22	28.72	31.42

Table 2: Error estimate (in %) for weight loss data.

Sample	Loss 1	Loss 2	Error
Methanol (Gas) Bulk Fly Ash	28.52	28.61	0.28
Water (Bicarbonate) Non-Magnetic	33.22	34.75	4.40

Table 3: Theoretical ranges for CO_2 loading for ashes originating from this power station (Weight %).

Carbon Dioxide Ranges	Maximum	Minimum
Unadjusted	25.18	14.02
Steinour	38.58	2.85
Steinour (No Sulfur)	41.12	17.13

The data in Table 1 show that the carbon dioxide loading of the CFA samples is on the order of 30% regardless of the solvent selected. (However, as discussed below, the methanol solvent yields carbonates that are more workable and less cementitious.) On the basis of our own analyses, the

Steinour formula (Eq. 6) predicts approximately 27% carbonation for the actual sample we investigated, which is in good agreement with the factual findings. The Steinour formula is designed to provide a quick assessment tool for the total carbonation potential of an ash sample and a loading of approximately 20 to 30% for this work was expected on the basis of this formula. The Steinour formula attempts to account for carbonation antagonizers such as the acidic sulfur oxides.[5] Other species interfering with carbonation are the acidic oxides of phosphorus and possibly nitrogen.

$$(6)\quad CO_2\,(\%) = 0.785\,(CaO - 0.7\,SO_3) + 1.09\,NaO + 0.93\,K_2O$$

With respect to the degree of carbonation, there are no substantial differences between water and methanol visible in the data and the likely reason is that the samples were carbonated exhaustively. The difference between the bicarbonate and the simulated flue gas numbers is attributed to the presence of residual bicarbonate reagent in the former. Comparison of the curves (Figures 1 and 2) shows that the respective CFA materials are different and the loss of fine structure in the weight loss profiles supports the presence of residual reagent in the final product. As a consequence, this demonstrates that it needs to be considered which supplemental reagents/bases can be added to the fly ash mix as there will be carry-over into the final product. There is a small difference between the magnetically enriched, the initial, and the magnetically depleted samples with respect to carbon loading. It appears that the magnetically enriched sample has a slightly lesser capability of CO_2 binding. While small, the difference is consistent throughout all conditions and suggests a reduction of binding capability of approximately 15% and indicates that iron oxides are not available for carbon binding. Iron oxide removal can be considered for high-iron-content ashes.

Based on verbal descriptions by laboratory personal, the samples changed appearance dramatically and substantial amounts of a grayish powder appeared during the exposure of the samples to CO_2. These observations suggest that the reaction of the ash with CO_2 was extensive and effective. The observations also indicate that the metal base was available outside of the sample particulate and that the pore limitations and surface effects observed in dry carbonations do not necessarily apply to slurry processes. Rephrased, in a dry carbonation process, the carbonation is limited to the accessibility of the alkaline metal oxide by the CO_2 through the particulate matrix, while in a slurry process the alkaline metal oxides are dispersed throughout the particulate and liquid components of the slurry.

In summary, these experiments establish that the carbonation of fly ash is readily and exhaustively affected in slurries on short time scales. However, a critical innovation of VCCS is the non-aqueous solvent, methanol, which plays an important role in the "workability" of the carbonated product, with methanol yielding a dry, workable product. In contrast, using water as a solvent yields a wet and cement-like carbonate product that is difficult to work with.

Trace Metals and Metal Leaching

Figures 3 through 6 at the end of this report give graphical representations of the trace metal data. Appendices 4 and 5 show the data in detail in tabulated form. What is clear from the data is that both purge gas and bicarbonate are extremely efficient in leaching metals from the ash on the allotted time scale of 15 minutes, thus confirming the metals extraction potential of the VCCS Cycle. In contrast, the current British standard method requires a two-stage leaching test of combined duration of 24 hrs for leachables of particulate solid wastes, including ashes. In essence, the time constraints suggested in the literature and in standard laboratory protocols for leaching are not relevant for the slurry process investigated herein. This is an extremely favorable outcome.

As expected, there is some preference among the metals toward specific solution conditions. Figure 7 shows the preferences for leaching under purge gas conditions with regard to the two investigated solvents and, in this data set, methanol exhibits better metal salt solvation as compared to water.

Overall, this study was effective in determining the fate of species during slurry carbonation and provided some answers to the leaching behavior of several metals during the VCCS process. Separate work is needed to show trends in a wider series of carefully selected metals. Once trends are identified, conditions can be modified to optimize the leaching profile of a slurry process leveraging the partitioning properties of methanol.

Future Work and Considerations

The results from this work demonstrate the feasibility of the VCCS Cycle in general, and therefore additional work to advance the Cycle toward commercialization is justified. Two items require particular attention: 1) the potential supplementation of the fly ash substrate by suitable materials to increase carbon dioxide removal from the flue gas; and 2) the exploitation and management of valuable metals contained in the fly ash as well as in supplemental substrates.

Additional sources of substrate for the Cycle will be identified and investigated. This might include the salvaging of existing waste piles of fly and bottom ash at the power plant, the pooling of ashes from multiple facilities, use of alkaline waste materials from water desalination, aluminum production, or mining and/or caustic soda production. Each possible supplemental substrate will be reviewed for suitability within the VCCS Cycle on the basis of chemical, ecological and economical aspects. For example, a power plant in close proximity to an aluminum production site may add alkaline aluminum production waste to the VCCS reactor to increase carbon capture from the power plant while providing a waste management solution for the aluminum production waste stream. Alkaline waste from other production processes may be considered as well, but clearly a review of alkaline waste sources is required. The key aspects are: What generates the waste? Where is the waste generated? What is it? Is it suitable for the Cycle? How does it affect the properties and application of the CFA? This is not an overwhelming task, but rather demonstrates the flexibility of the Cycle to provide solutions in addition to carbon remediation and fly ash management at the power station, and many such applications may be identified on a case-by-case basis.

Recovery of hazardous and/or valuable metals from the fly ash is a second, but important, consideration. At this point, tests need to be performed to gain a better understanding of metals recovery using a broader list of elements. When properly designed, such a study will provide the basis for predicting the metals recovery capacity of VCCS. In general, the usefulness of metals removal is twofold: 1) the generation of a more environmentally benign CFA material; and 2) the potential use of the concentrated metals waste in the recovery of rare and important metals.

It is possible that VCCS may also be effective for removing sulfur and mercury from flue gas, which would add to the total value of VCCS deployments. Expansion Energy plans future work to investigate the efficacy of VCCS for those applications.

Conclusions

The laboratory results demonstrate that the proposed VCCS Cycle is feasible. The methanolic slurry process will produce completely carbonated fly ash and is effective in removing leachable metals from the ash particulate. The recovery of certain trace metals is remarkably good—including many rare and valuable metals. This process will also remove the theoretically possible amount of CO_2 from the flue gas depending on CaO content, in this example 0.28 tons of CO_2 per 1 ton of fly ash. The data and observations to date also validate the selection of methanol as the slurry solvent. The actual minimum amount of water required for the process needs to be determined in an additional investigation.

Once metals are removed from the particulate, further enrichment and subsequent purification can be accomplished quite readily with existing industrial processes. Economic considerations will determine the application of the process. The conversion of the fly ash stream from a waste stream to a revenue stream, and the possibility of revenue from valuable metals, will offset some or all expenses of the VCCS process on the whole. General criteria for process deployment might include the hazard level of fly ash, waste disposal options at the power plant location, the pending categorization of coal-based fly ash as "hazardous waste" by the US EPA (or other regulatory body), and the original source and composition of the coal.

Extending the scope of the VCCS Cycle to the treatment of the ashes from municipal waste incineration would be an intriguing application as well, in part because levels of environmentally relevant metals are high in municipal waste streams, and because emission and landfill directives are more stringent for such facilities. This treatment allows for the reduction of leachable metals from the fly ash substrate and allows for the safe disposal of the hazardous components.

In addition to carbon capture & sequestration plus fly ash management applications, VCCS may also find applications as a clean-up process for the feed gases utilized by natural gas processing plants, LNG liquefaction plants, anaerobic digester gas (ADG) facilities, landfill gas (LFG) facilities, and plants that produce industrial gases. VCCS can remove large concentrations of CO_2 and water (and possibly H_2S) from feed gases. VCCS may be especially valuable for feed gas that is particularly "dirty," such as untreated field gas (e.g., at wellheads), ADG and LFG, and where traditional clean-up systems such as molecular sieves or membrane systems may be too expensive or not robust enough to handle high levels of impurities.

Further Materials and Discussion

Appendix 6 is a worksheet for reference and planning purposes for further investigation and analysis. Appendix 6 is a nearly comprehensive alphabetical listing of chemical elements in coal. Its purpose is to provide a basis for screening regarding hazardous and high-value metals that may be recovered in the VCCS Cycle—thereby increasing the economic value of coal and coal ash, while reducing its environmental impact. The "Typical" Coal, Bottom Ash (BA) and Fly Ash (FA) columns reflect the concentration level of an element a laboratory would calibrate analytical equipment for on the basis of industry-standard test methods and empiricism. As an implication, these numbers are a good guideline for what to expect from a coal or fly ash sample, but regional or coal origin variations need to be investigated. The columns headed "Literature" contain values from a variety of literature sources compiled for this report and do not represent an exhaustive effort underlining the significance of regional variations. These values do not necessarily match the values reported in other columns as they are of different background and source.

The "This Study" columns show chemical element levels obtained in this study for leached metals and carbonated fly ash. For the purpose of further discussion and planning, columns titled "'Green' Metal", "Energy Metal" and "Worthwhile" were included. The "green" metals are generally "rare earth elements" that are critical raw materials for advanced energy saving, energy storage and energy generation technologies, such as hybrid cars, solar panels, wind turbine components/electronics, and electricity storage (e.g., advanced batteries). The Energy Metal category marks elements utilized in the nuclear energy sector for power generation. "Worthwhile" elements represent a collection of metals that have high economic value in general, but were not grouped into the two other categories. These columns are comprehensive, but entries will require project-based updating from further investigations. It should be realized that Appendix 6 is a true worksheet.

Figure 1: Example TGA Curve Shown as Differential Plot of Time (s) *vs.* Loss.[i]

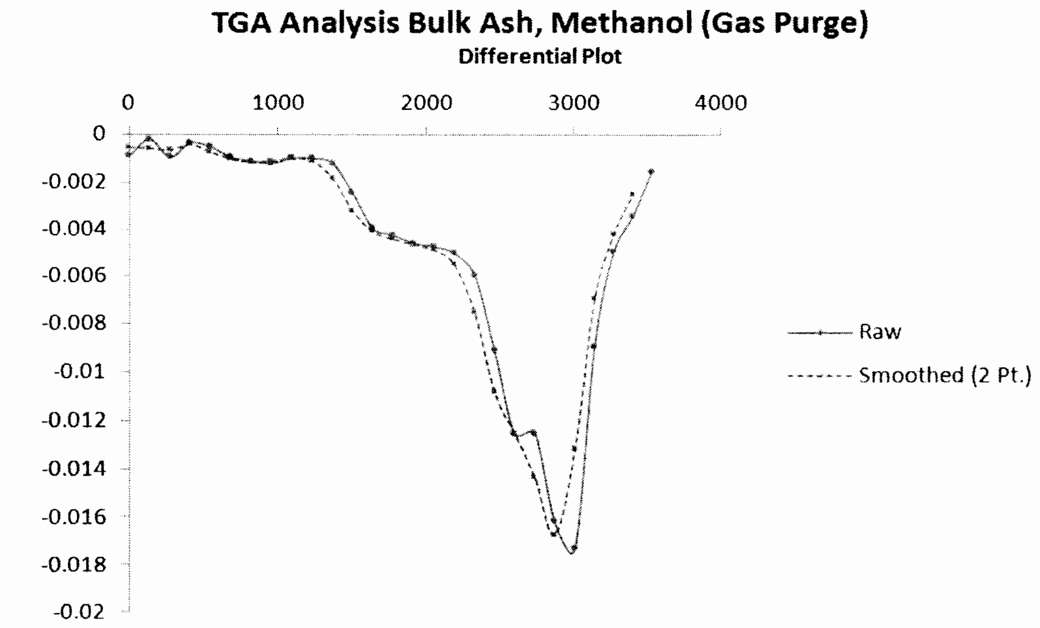
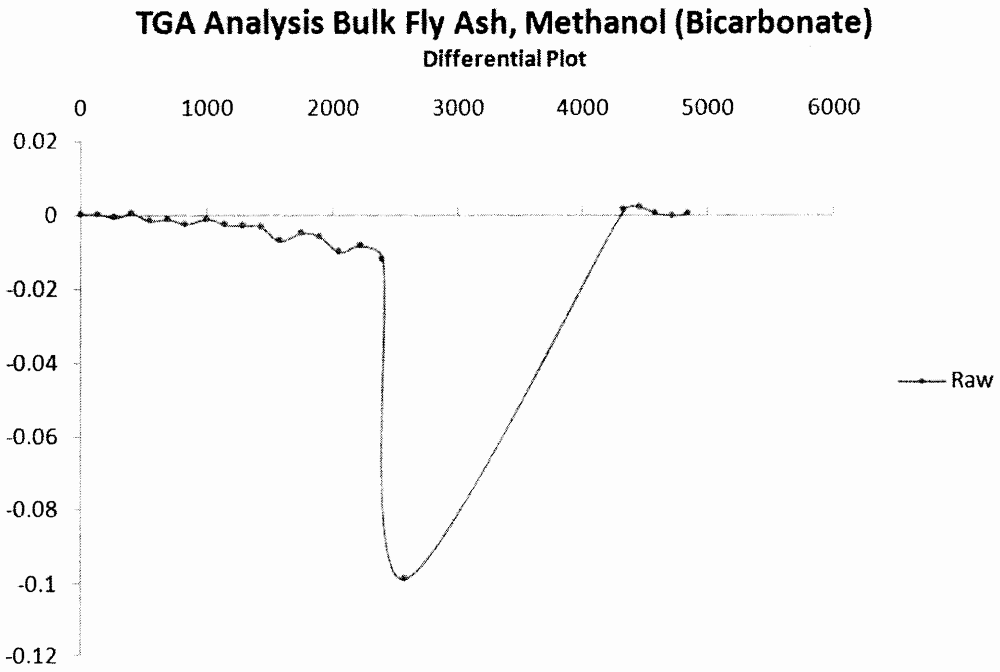


Figure 2: Example TGA Curve Shown as Differential Plot of Time (s) *vs.* Loss.



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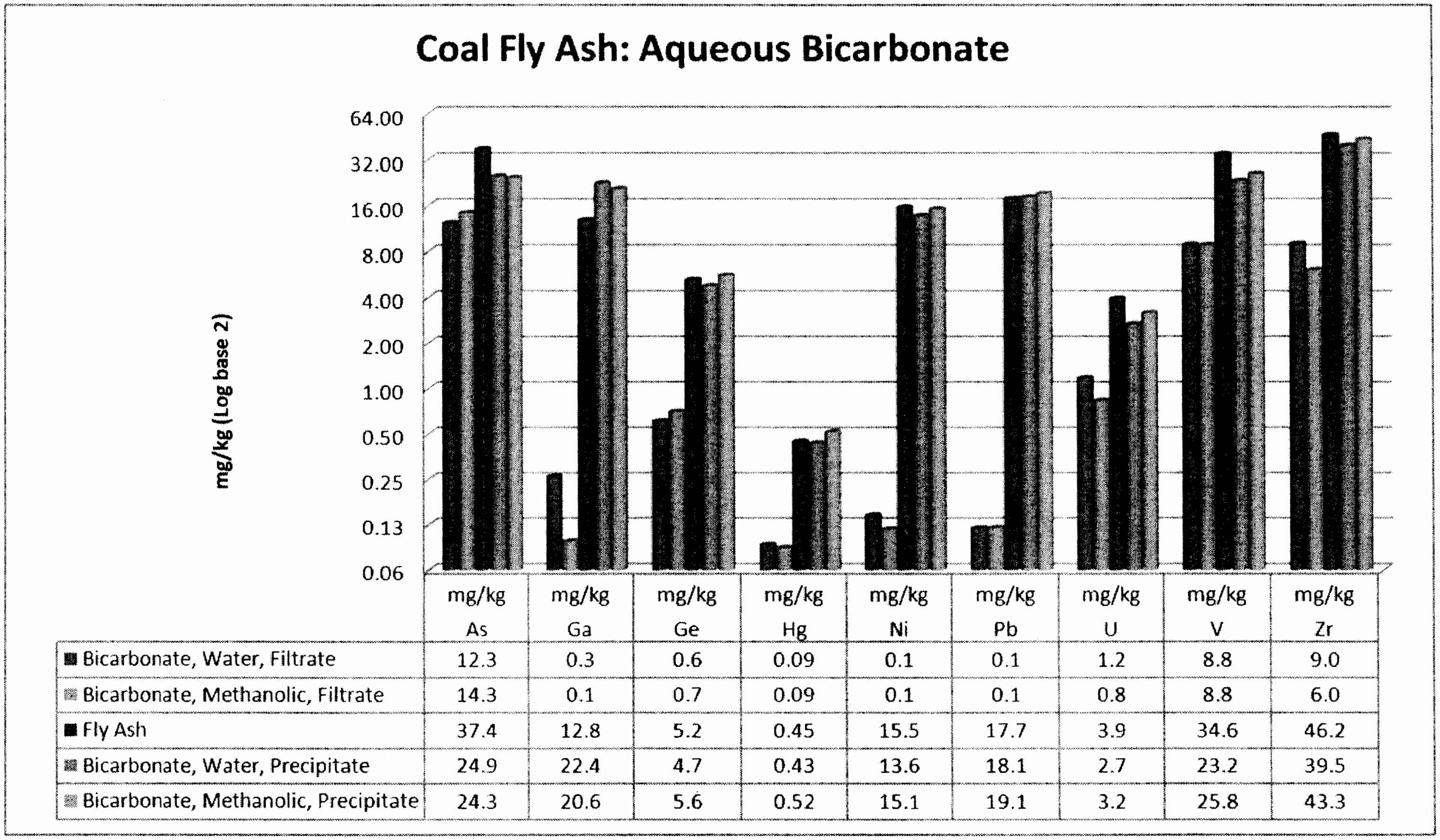
[i] Differential determined as Value (Time 1) – Value (Time 2); smoothed data curve is 2-point moving average.

Figure 3: Representation of ICP-MS Data for Trace Metals Distribution under Bicarbonate Conditions as Log Base 2 Plot.[i]



	mg/kg As	mg/kg Ga	mg/kg Ge	mg/kg Hg	mg/kg Ni	mg/kg Pb	mg/kg U	mg/kg V	mg/kg Zr
■ Bicarbonate, Water, Filtrate	12.3	0.3	0.6	0.09	0.1	0.1	1.2	8.8	9.0
▨ Bicarbonate, Methanolic, Filtrate	14.3	0.1	0.7	0.09	0.1	0.1	0.8	8.8	6.0
■ Fly Ash	37.4	12.8	5.2	0.45	15.5	17.7	3.9	34.6	46.2
▨ Bicarbonate, Water, Precipitate	24.9	22.4	4.7	0.43	13.6	18.1	2.7	23.2	39.5
▨ Bicarbonate, Methanolic, Precipitate	24.3	20.6	5.6	0.52	15.1	19.1	3.2	25.8	43.3

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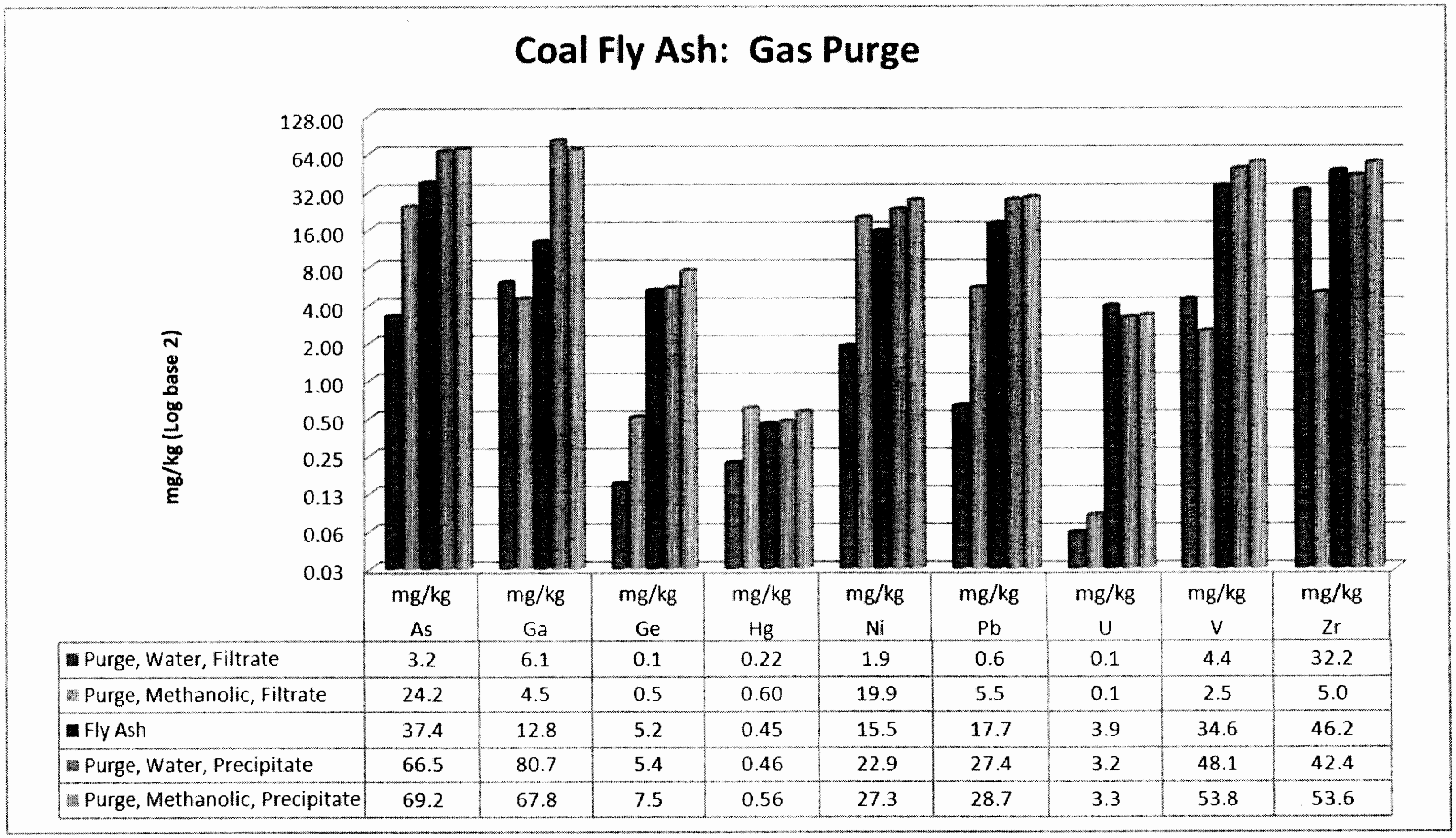
[i] In this chart, "Filtrate" refers to the solvent containing the leachable, and "Precipitate" refers to the carbonated fly ash.

Figure 4: Representation of ICP-MS Data for Trace Metals Distribution under Purge Gas Conditions as Log Base 2 Plot.[i]



	mg/kg As	mg/kg Ga	mg/kg Ge	mg/kg Hg	mg/kg Ni	mg/kg Pb	mg/kg U	mg/kg V	mg/kg Zr
■ Purge, Water, Filtrate	3.2	6.1	0.1	0.22	1.9	0.6	0.1	4.4	32.2
▨ Purge, Methanolic, Filtrate	24.2	4.5	0.5	0.60	19.9	5.5	0.1	2.5	5.0
■ Fly Ash	37.4	12.8	5.2	0.45	15.5	17.7	3.9	34.6	46.2
▨ Purge, Water, Precipitate	66.5	80.7	5.4	0.46	22.9	27.4	3.2	48.1	42.4
▨ Purge, Methanolic, Precipitate	69.2	67.8	7.5	0.56	27.3	28.7	3.3	53.8	53.6

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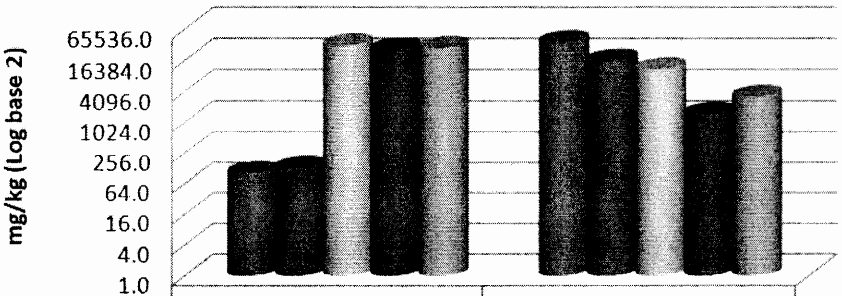
[i] In this chart, "Filtrate" refers to the evaporated solvent containing the leachable, and "Precipitate" refers to the carbonated fly ash.

Figure 5: Representation of ICP-MS Data for Iron and Sulfur Distribution under Bicarbonate Conditions as Log Base 2 Plot.[i]

Coal Fly Ash: Aqueous Bicarbonate



	mg/kg Fe	mg/kg S
■ Bicarbonate, Water, Filtrate	106.3	36950.0
■ Bicarbonate, Methanolic, Filtrate	134.7	16233.3
▨ Fly Ash	32266.7	11100.0
■ Bicarbonate, Water, Precipitate	26533.3	1510.0
▨ Bicarbonate, Methanolic, Precipitate	28900.0	3250.0

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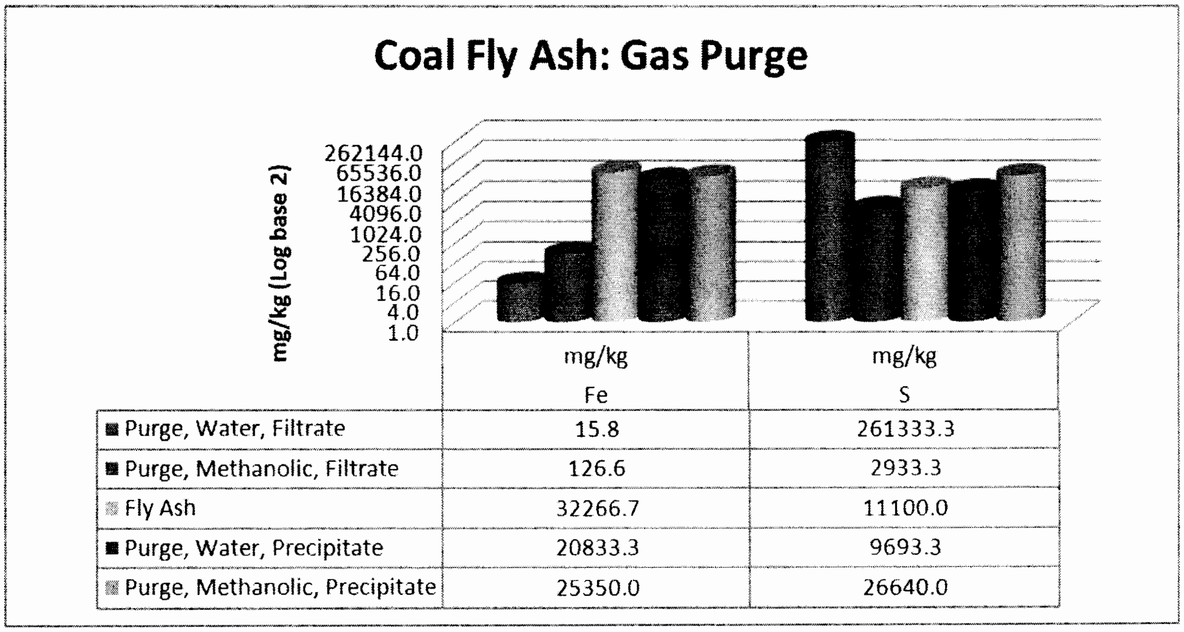
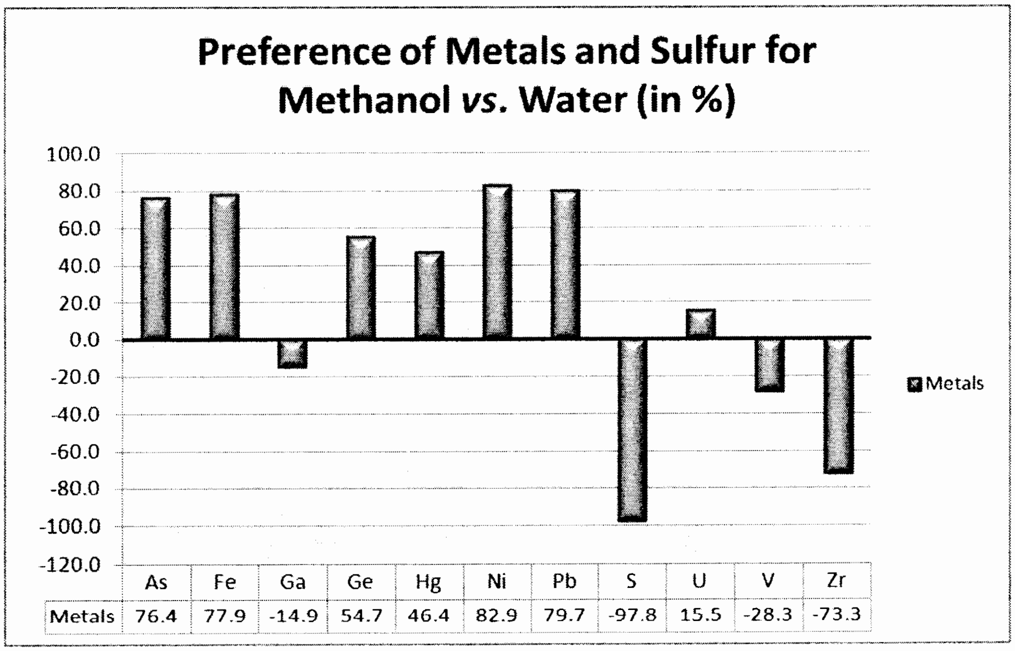
[i] In this chart, "Filtrate" refers to the solvent containing the leachable, and "Precipitate" to the carbonated fly ash.

Figure 6: Representation of ICP-MS Data for Iron and Sulfur Distribution under Purge Gas Conditions as Log Base 2 Plot.[i]



	mg/kg Fe	mg/kg S
■ Purge, Water, Filtrate	15.8	261333.3
■ Purge, Methanolic, Filtrate	126.6	2933.3
▨ Fly Ash	32266.7	11100.0
■ Purge, Water, Precipitate	20833.3	9693.3
▨ Purge, Methanolic, Precipitate	25350.0	26640.0

Figure 7. Relative Partitioning of Selected Trace Elements and Preference for Methanol.[i]



	As	Fe	Ga	Ge	Hg	Ni	Pb	S	U	V	Zr
Metals	76.4	77.9	-14.9	54.7	46.4	82.9	79.7	-97.8	15.5	-28.3	-73.3

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[i] Positive values indicate preference for methanol.

Appendix 1: Statistical Evaluation of North Dakota Coal (USGS Data) and Comparison with Fly Ash Data (ppm, this report).

Element	Si	Al	Ca	Mg	Na	K	Fe	Ti	S	Ag	As	Au	B	Ba	Be
USGS[i]	23.0[ii]	9.1[ii]	15.4[ii]	5.5[ii]	5.2[ii]	0.5[ii]	8.6[ii]	0.6[ii]	17.1[ii]	0.08	8.42	0.60	129.55	680.25	0.92
FA[iii]	23.8[ii]	10.4[ii]	25.4[ii]	6.8[ii]	5.9[ii]	0.6[ii]	7.3[ii]	0.4[ii]	14.6[ii]		37.2				
Element	Bi	Br	Cd	Ce	Cl	Co	Cr	Cs	Cu	Dy	Er	Eu	F	Ga	Gd
USGS	1.05	0.00	0.11	11.42	110.00	2.69	6.78	NR[iv]	6.95	2.69	0.49	0.17	32.99	3.11	2.20
FA														4.8	
Element	Ge	Hf	Hg	Ho	In	Ir	La	Li	Lu	Mn	Mo	Nb	Nd	Ni	Os
USGS	2.55	6.15	0.13	0.88	3.17	3.27	7.38	3.53	1.31	84.39	3.83	2.40	7.85	3.98	1.93
FA	5.2		0.45		ND[v]									15.5	
Element	Os	P	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	Sb	Sc	Se	Sm	Sn
USGS	1.93	293.31	3.66	0.11	8.95	0.64	NR	3.01	0.23	0.64	0.58	1.98	0.79	3.01	0.52
FA			17.7												
Element	Sr	Ta	Tb	Te	Th	Tl	Tm	U	V	W	Y	Yb	Zn	Zr	
USGS	334.37	43.16	4.16	NR	2.23	0.77	0.49	1.53	11.93	3.27	6.49	0.64	10.90	22.40	
FA								3.9	34.6					46.2	

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[i] USGS data based on coal except as noted.

[ii] Data in % based on ash.

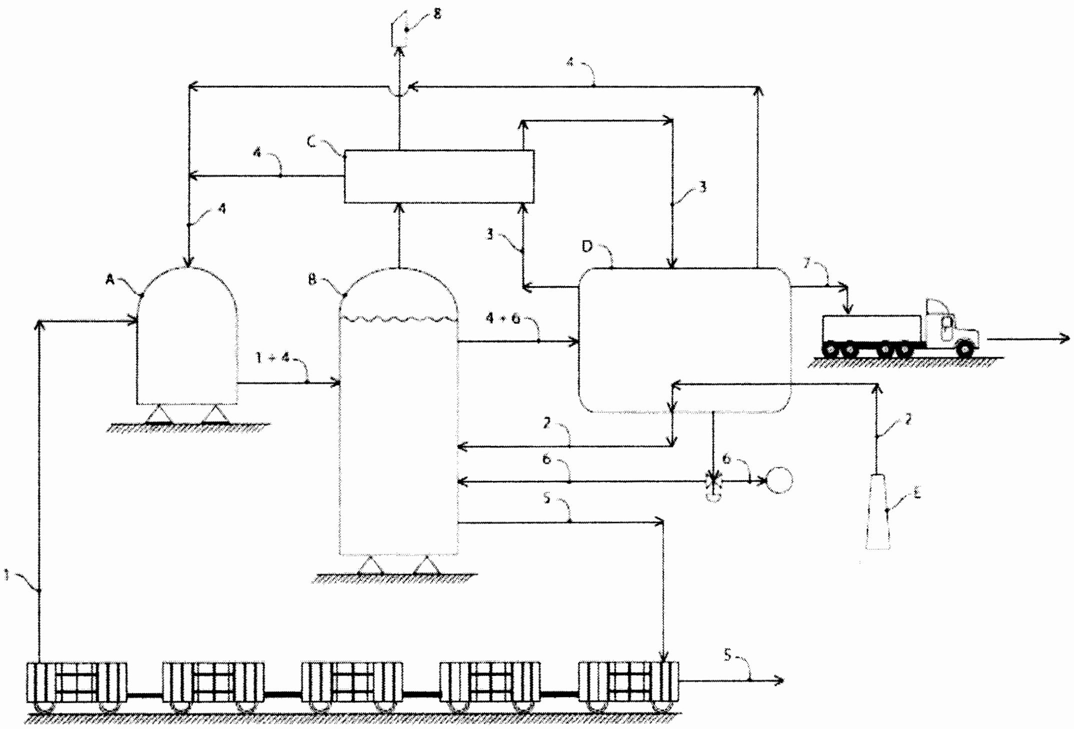
[iii] FA: Fly ash, this study. Values in % extrapolated from data communicated by Expansion Energy LLC.

[iv] NR: Not Reported

[v] ND: Not Detected

Appendix 2. Schematic Diagram of the VCCS™ Cycle

US Patents No. RE 45,309 (7,947,240); 8,252,242 and 8,501,125
Japan Patent No. 4880098
Canada Patent No. 2,739,743 and 2,836,239
Australia Patent No. 2009302737 and 2012256278
China Patent No. 200980149295.6
+
Additional International Patents Pending



KEY

MAJOR COMPONENTS
A - MIXING VESSEL
B - REACTION VESSEL
C - METHANOL CONDENSER
D - METHANOL REGENERATION + WATER DESALINATION
E - POWER PLANT FLUE

INFLOW STREAMS
1 - ASH + OPTIONAL ALKALI
2 - WARM FLU GAS CO_2, N_2, AR, O_2...
3 - ABSORPTION REFRIGERATION
4 - METHANOL

OUTFLOW STREAMS
5 - DRY CARBONATES, IRON OXIDE, SAND...
6 - WATER
7 - SALTS + RARE EARTH COMPOUNDS
8 - REDUCED - CO_2 FLUE GAS

Appendix 3: Study Protocol for Fly Ash Analysis.

Test Plan:

a. Materials:

   i. Fresh fly ash (lignite North Dakota)

   ii. Magnetic fly ash components

   iii. Non-magnetic fly ash components

   iv. 95% methanol

   v. di-Water

   vi. Sodium bicarbonate (Metal Analysis grade)

b. Reagents:

   i. Reagent R: 1 L of a 5 w% solution of sodium bicarbonate in di-water.

   ii. Reagent S: 1 L of aqueous carbonate solution (pH = 5.6).

c. Titration parameters:

   i. Potentiometric pH determination of aqueous and methanolic slurries:

   Starting at time t = 300 s, every 30 s are added 2.5 mL of R to the samples C and D. Temperature is determined within 5 sec after addition and the pH is determined 25 s after addition. Additions are continued every 30 s to time point 1200 s. The last temperature is determined at t = 1205 s and the last pH is determined at t = 1225 s.

d. Experiments (titration):

   i. 20 mL of 95% methanol (Sample A) and separately 20 mL of di-Water (Sample B) are placed in a suitable glass vessel and the pH(pS) and the solution temperature are determined and recorded. Subsequently, 50 mL of R are added to each and the pH(pS) and the solution temperature are determined and recorded. Also, any visible changes to the solutions are to be documented.

   ii. At t = 0 sec, 5 g of fly ash are slurried in 20 mL of 95% methanol (Sample C) and the pH(pS) and temperature of the solution are determined and recorded. Titrate according to c.i. The mixture is filtered and the filter cake washed with 20 mL of 95% methanol. The filtrate and washings are combined and reduced to dryness. The weight of the residue is recorded. The filter cake is allowed to air dry overnight and the weight is recorded.

iii. At t = 0 sec, 5 g of fly ash are slurried in 20 mL of di-water (Sample D) and the pH and temperature of the solution are determined and recorded. Titrate according to c.i. The mixture is filtered and the filter cake washed with 20 mL of di-water. The filtrate and washings are combined and reduced to dryness. The weight of the residue is recorded. The filter cake is allowed to air dry overnight and the weight is recorded.

iv. A 2 g sample of each of the filter cakes (d.ii. and d.iii.) are slurried in 20 mL of pH 5.6 water for 5 minutes, filtered and subsequently washed with 20 mL of di-water. The filtrate and washings are combined and the pH is determined. The filter cake is allowed to air dry overnight and the weight is determined.

v. Samples of the filter cakes (d.ii. and d.iii.) are dried at 105 °C for 5 hours. These samples are submitted to TGA. Temperature range ambient to 850 °C. Details will be discussed with the testing laboratory.

e. Experiments (gassed)

i. 20 mL of 95% methanol (Sample A) and separately 20 mL of di-Water (Sample B) are placed in a suitable glass vessel and the pH(pS) and the solution temperature are determined and recorded. Subsequently, simulated flue gas is purged through the solutions for 10 min. pH(pS) and temperature are determined again within 1 min of the end of gas flow.

ii. At t = 0 sec, 5 g of fly ash are slurried in 20 mL of 95% methanol (Sample E) and the pH(pS) and temperature of the solution are determined and recorded. Simulated flue gas will be purged through the solution from t= 300 to 900 s and the flow rate is monitored. pH(pS) and temperature readings will be acquired every 30 s. The mixture is filtered and the filter cake washed with 20 mL of 95% methanol. The filtrate and washings are combined and reduced to dryness. The weight of the residue is recorded. The filter cake is allowed to air dry overnight and the weight is recorded.

iii. At t = 0 sec, 5 g of fly ash are slurried in 20 mL of di-water (Sample F) and the pH and temperature of the solution are determined and recorded. Simulated flue gas will be purged through the solution from t= 300 to 900 s and the flow rate is monitored. pH and temperature readings will be acquired every 30 s. The mixture is filtered and the filter cake washed with 20 mL of di-water. The filtrate and washings are combined and reduced to dryness. The weight of the residue is recorded. The filter cake is allowed to air dry overnight and the weight is recorded.

iv. A 2 g sample of each of the filter cakes (e.ii. and e.iii.) are slurried in 20 mL of pH 5.6 water for 5 minutes, filtered and subsequently washed with 20 mL of di-water. The filtrate and washings are combined and the pH is determined. The filter cake is allowed to air dry overnight and the weight is determined.

v. Samples of the filter cakes (e.ii. and e.iii.) are dried at 105 °C for 5 hours. These samples are submitted to TGA. Temperature range ambient to 850 °C. Details will be discussed with the testing laboratory.

f. Metals Panel

i. The filtrate residues (d.ii., d.iii., e.ii. and e.iii.), filter cakes (d.ii, d.iii., e.ii., and e.iii.), and fly ashes (a.i., a.ii., a.iii.) are submitted to a metals panel by ICP/MS. Target metals are Fe, Ni, V, Pb, Hg, U, Ge, As, Ga, In, and Zr. Elements to include are S.

Appendix 4: Compiled ICP-MS Data for Bicarbonate Conditions. Data Shown for Completeness.

	As	Fe	Ga	Ge	Hg	Ni	Pb	S	U	V	Zr
Sample ID	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
L8444-DI-R-F (residue)[i]	12.5	114	0.301	0.737	0.098	0.129	0.085	36,300	1.17	9.08	9.35
L8445-DI-R-F (residue)	12.3	76.9	0.232	0.485	0.091	0.151	0.118	37,700	1.15	8.93	8.27
L8446-DI-R-F (residue)	12.0	128	0.245	0.593	0.087	0.152	0.152	36,850	1.19	8.49	9.31
L8444-MeOH-R-F (residue)	13.2	84.6	0.080	0.628	0.083	0.112	0.071	18,000	0.934	8.70	7.69
L8445-MeOH-R-F (residue)	14.8	233	0.122	0.761	0.091	0.130	0.128	15,400	0.773	8.61	4.98
L8446-MeOH-R-F (residue)	14.8	86.4	0.089	0.71	0.089	0.107	0.158	15,300	0.783	9.09	5.44
L8444-initial	39.2	28,000	10.6	4.16	0.405	15.7	17.9	10,800	3.94	36.6	44.3
L8445-initial	38.3	45,000	14.9	6.73	0.441	17.0	17.3	11,600	3.97	34.3	49.9
L8446 initial	34.6	23,800	12.9	4.72	0.491	13.8	17.9	10,900	3.83	32.9	44.5
L8444-DI-R-C1 [ii]	24.0	23,000	23.0	4.07	0.424	13.0	17.4	1,540	2.63	22.3	40.0
L8445-DI-R-C1	27.2	36,300	20.7	5.84	0.435	14.7	18.8	1,400	2.81	24.2	40.9
L8446-DI-R-C1	25.6	29650	21.85	4.955	0.4295	13.85	18.1	1470	2.72	23.25	40.45
L8444-MeOH-R-C1	23.9	25,400	21.9	4.99	0.5	14.4	18.6	2,830	2.99	24.7	40.2
L8445-MeOH-R-C1	26.0	37,400	20.6	6.81	0.587	16.9	19.9	3,520	3.41	27.1	47.1
L8446-MeOH-R-C1	23.1	23,900	19.2	4.85	0.462	14.0	18.9	3,400	3.07	25.7	42.7

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[i] “residue” refers to the dissolved matter in the solvent. This is where the leachables are.

[ii] Entries ending in “-R-C1” identify carbonated fly ash.

Appendix 5: Compiled ICP-MS Data for Purge Gas Conditions. Data Shown for Completeness.

	As	Fe	Ga	Ge	Hg	Ni	Pb	S	U	V	Zr
Sample ID	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
L8444-DI-P-F (residue)[i]	3.23	16.6	12.1	0.171	0.230	1.98	0.84	245000	0.018	4.79	31.1
L8445-DI-P-F (residue)	4.32	16.5	4.15	0.164	0.266	1.34	0.55	301400	0.15	7.52	39.9
L8446-DI-P-F (residue)	2.16	14.2	1.90	0.108	0.158	2.27	0.47	237600	0.014	0.87	25.5
L8444-MeOH-P-F (residue)	35.5	93.8	3.04	0.224	0.620	15.7	5.78	3856	0.076	2.84	3.97
L8445-MeOH-P-F (residue)	23.0	173	4.95	0.902	0.518	22.0	5.16	1723	0.093	2.36	6.13
L8446-MeOH-P-F (residue)	14.1	113	5.46	0.386	0.650	22.0	5.5	3221	0.08	2.16	4.79
L8444-initial	39.2	28,000	10.6	4.16	0.405	15.7	17.9	10,800	3.94	36.6	44.3
L8445-initial	38.3	45,000	14.9	6.73	0.441	17.0	17.3	11,600	3.97	34.3	49.9
L8446 initial	34.6	23,800	12.9	4.72	0.491	13.8	17.9	10,900	3.83	32.9	44.5
L8444-DI-P-C1 [ii]	59.0	16300	77.1	4.67	0.47	21.1	27.9	6718	3.10	47.6	37.8
L8445-DI-P-C1	67.8	28700	86.4	7.64	0.47	25.3	27.6	7722	3.22	47.9	42.7
L8446-DI-P-C1	72.8	17500	78.6	4.00	0.45	22.3	26.8	14640	3.16	48.9	46.6
L8444-MeOH-P-C1	70.3	23100	82.5	5.82	0.46	23.8	27.2	11181	3.19	48.4	44.65
L8445-MeOH-P-C1	78.2	36200	77.4	10.8	0.66	26.1	29.8	27750	3.20	54.1	58.1
L8446-MeOH-P-C1	62.2	19300	60.8	6.33	0.56	26.0	27.8	27500	3.30	54.1	50.3

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[i] "residue" refers to the dissolved matter in the solvent. This is where the leachables are

[ii] Entries ending in "-R-C1" identify carbonated fly ash.

Appendix 6: Element Worksheet for Coal with Metal Value/Use Designations

Method	Element	Cont.	Typ. Coal	Typ. BA	Typ. FA	Coal Literature Ranges	Ash Literature Ranges	This Study - Filtrate	This Study - FA	"Green" Metal	Energy Metal	Worth-while
NAA	Aluminum (Al)	%	3.53	8.58	13.1							
NAA	Antimony (Sb)	ppm	0.68	0.8	3.5	10 - 30	100 - 3000					
NAA	Arsenic (As)	ppm	2.3	2.7	14.2	0.8 - 500	280 - 10000	24.2	37.4			
NAA	Barium (Ba)	ppm	761	1580	3320	2 - 257	18 - 2200					
ICPMS	Beryllium (Be)	ppm	1.1	1.9	3.2	0.1 - 40	1 - 4000					
ICPMS	Bismuth (Bi)	ppm	0.19	0.12	0.7	0 - 100	0 - 2000					
PG	Boron (B)	ppm	48	143	353	15 - 356	52 - 10000					
NAA	Bromine (Br)	ppm	0.9	1	1.1							
ICPMS	Cadmium (Cd)	ppm	0.09	0.06	0.32							
NAA	Calcium (Ca)	%	1.37	3.49	7.41							
NAA	Cerium (Ce)	ppm	32	73	134					X		
NAA	Cesium (Cs)	ppm	0.6	1.4	2.7							
NAA	Chlorine (Cl)	ppm	<28	<45	<61							
NAA	Chromium (Cr)	ppm	6	30	28	<0.1 - 50	<0.1 - 7400					
NAA	Cobalt (Co)	ppm	2.2	5.4	9.9	0.4 - 34	5 - 2000					
ICPMS	Copper (Cu)	ppm	5.6	16	22	2.6 - 85	10 - 1200					
NAA	Dysprosium (Dy)	ppm	2.1	4.7	7.6					X		
	Erbium (Er)									X		
NAA	Europium (Eu)	ppm	0.41	0.9	1.6					X		
	Gadolinium	ppm								X		
NAA	Gallium (Ga)	ppm	11	17	32	1.2 - 100	10 - 3200	4.5	12.8			X
ICPMS	Germanium (Ge)	ppm	0.4	0.6	2.4	0.4 - 50	9 - 47000	0.5	5.2			X
NAA	Gold (Au)	ppb	<1	<3	<5							X
NAA	Hafnium (Hf)	ppm	2.5	6.1	10.8					X		

Appendix 6: Element Worksheet for Coal with Metal Value/Use Designations (cont.)

Method	Element	Cont.	Typ. Coal	Typ. BA	Typ. FA	Coal Literature Ranges	Ash Literature Ranges	This Study - Filtrate	This Study - FA	"Green" Metal	Energy Metal	Worth-while
	Holmium (Ho)										X	X
NAA	Indium (In)	ppm	<0.04	<0.06	0.09					X		X
NAA	Iodine (I)	ppm	<1	<2	3					X		X
NAA	Iridium (Ir)	ppb	<1	<3	<4					X		
NAA	Iron (Fe)	%/ppm	0.48	1.7	2.48			126.6	32266.7			
NAA	Lanthanum (La)	ppm	20	43	75	1.5 - 40	<30 - 700			X		
ICPMS	Lead (Pb)	ppm	12.9	15.5	49	25 - 3000	200 - 31000	5.5	17.7			
ICPMS	Lithium (Li)	ppm	12.1	25.4	6.4					X		
NAA	Lutetium (Lu)	ppm	0.17	0.39	0.71					X		
NAA	Magnesium (Mg)	%	0.1	0.25	0.57							
NAA	Manganese (Mn)	ppm	71	286	388	9 - 5000	100 - 22000					
NAA	Mercury (Hg)	ppm	0.08	<0.1	<0.2	<0.1 - 300		0.60	0.45			
NAA	Molybdenum (Mo)	ppm	2.1	15	8.2	<0.7 - 200	<5 - 6000					
NAA	Neodymium (Nd)	ppm	10	25	45					X		
ICPMS	Nickel (Ni)	ppm	5.1	13	15	0.42 - 60	5 - 16000	19.9	15.5			
ICPMS	Niobium (Nb)	ppm	4.7	14	22					X		
	Palladium (Pd)											X
ICPMS	Phosphorus (P)	ppm	67	230	310							
	Platinum (Pt)											X
NAA	Potassium (K)	%	0.14	0.31	0.65							
NAA	Rubidium (Rb)	ppm	6	15	33							X
NAA	Samarium (Sm)	ppm	2.3	5.6	9.9					X		
NAA	Scandium (Sc)	ppm	3	6.6	13.1		60 - 400			X		

Appendix 6: Element Worksheet for Coal with Metal Value/Use Designations (cont.)

Method	Element	Cont.	Typ. Coal	Typ. BA	Typ. FA	Coal Literature Ranges	Ash Literature Ranges	This Study - Filtrate	This Study - FA	"Green" Metal	Energy Metal	Worth-while
NAA	Selenium (Se)	ppm	0.5	<1	2							
	Silicon (Si)											
NAA	Silver (Ag)	ppm	<0.3	<1	<1	0 - 3	0 - 60					X
NAA	Sodium (Na)	%	0.38	0.64	1.81							
ICPMS	Strontium (Sr)	ppm	155	385	713	0 - 100	0 -1000					
NAA	Tantalum (Ta)	ppm	0.61	1.5	2.5							X
ICPMS	Tellurium (Te)	ppm	<0.06	<0.05	0.15							X
NAA	Terbium (Tb)	ppm	0.3	0.7	1.2					X		
ICPMS	Thallium (Tl)	ppm	0.09	0.1	0.58							X
NAA	Thorium (Th)	ppm	7.99	18	31						X	
	Thulium											X
NAA	Tin (Sn)	ppm	<15	<50	<67	0.1 - 300	0.4 - 6000					
NAA	Titanium (Ti)	%/ppm	0.091	0.22	0.38	95 - 2300	100 - 35000					
NAA	Tungsten (W)	ppm	1	1.8	3.1							
NAA	Uranium (U)	ppm	3.3	7.7	14	0 - 24000	6 - 1650	0.1	3.9		X	
NAA	Vanadium (V)	ppm	13	26	60	<1.4 - 100	10 - 25000	2.5	34.6			X
NAA	Ytterbium (Yb)	ppm	1.1	2.6	4.6					X		
ICPMS	Yttrium (Y)	ppm	9.5	20	36	0.1 - 49	10 - 2000			X		
NAA	Zinc (Zn)	ppm	23	16	46	7 - 2000	115 -21000					
NAA	Zirconium (Zr)	ppm	<35	70	110	0 - 140	0 - 7000	5.0	46.2			

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