PROJECT PROPOSAL

Submitted by

Mattoon Power Enterprises LLC

in collaboration with

Great River Energy,

with support from

Basin Electric Power Cooperative

and

North American Coal Corporation

TO TEST, CONFIRM, AND INITIATE COMMERCIAL DESIGN OF A POST-COMBUSTION "BOLT-ON" CO₂ CAPTURE SYSTEM SUITABLE FOR AT-SCALE, ROYALTY-FREE RETROFIT OF EXISTING NORTH DAKOTA LIGNITE- AND COAL-FIRED POWER GENERATING FACILITIES (WITH NORTH DAKOTA MANUFACTURING OPPORTUNITY TO REACH NATIONAL AND INTERNATIONAL MARKETS).

Submitted to the North Dakota Lignite Energy Council,

Lignite Research, Development and Marketing program

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Abstract

Objectives: A focus of the proposed work is to demonstrate and measure the effectiveness of new methods for a cost effective "bolt-on" solution capable of reducing the cost of CO_2 capture for 60% - 90% of the CO_2 in coal and lignite flue gas. The approach is based on technical innovations for a proven potassium carbonate process to operate at atmospheric and near-atmospheric conditions, and a broader view of the overall economics, which include benefits to North Dakota in its lignite, coal, energy production, and manufacturing sectors, as described more specifically in the proposal.

The successful conduct of the proposed project is expected to provide immediate, direct benefit to North Dakota in the following, summary areas:

- Mattoon Power Enterprises ("MPE", "we") expect(s) the carbon capture system developed will provide a basis for existing coal- and lignite-fired generating facilities to secure atmospheric CO₂ capture capabilities under any current or anticipated "clean coal" regulatory regime;
- The carbon capture system developed will enable maintenance and expansion of current lignite and coal markets, as well as provide manufacturing opportunities within the state;
- MPE will offer North Dakota entities license-free use of MPE commercialized systems deployed by on a perpetual royalty-free basis;
- MPE will allocate agreed percentages of its initially-received commercial revenues to repay all grant funding received from North Dakota.

Achievability: Currently there are three commercially available technologies that can daily capture thousands of tons of flue gas CO_2 . These are based on either carbonate, amine or ammonia-based absorption / desorption processes. MPE's potassium carbonate (K_2CO_3) system offers several important benefits over amine-based systems including low material and operating costs, freedom from chemical degradation, avoidance of corrosion, fire and safety hazards. MPE anticipates that its proprietary K_2CO_3 process will lower the CO_2 capture cost, an effect enhanced by current tax provisions under the "45Q" designation. The project will involve utilization of an MPE test facility that has previously demonstrated the efficient and economical capture of CO_2 from pressurized combustion systems.

Contribution: The proposed project activities will provide the basis for a commercial opportunity to capture CO_2 at economically feasible lower pressures.

Awareness and Background of MPE Team: MPE team members, identified and described fully at *Qualifications* (below, page 24), have a detailed understanding of the underlying physical and chemical processes, the current scientific literature, and other state-of-the-art processes for CO₂ capture. All team members have been involved in the design, commissioning and successful operation of complex, industrial scale, chemical processes, including systems for the capture of CO₂. Participants and Project Management.

Project Summary

This section, as required by the Lignite Energy Council, provides an overview to help the Lignite Council select external reviewers for the proposal. This Project Summary provides a brief description of proposed tasks together with anticipated deliverables and an appendix that describes the previous experience in using the test rig on a coal fired power plant.

Introduction

MPE is confident that the proposed project will establish that a bolt-on module for capture of CO_2 from coal- or lignite-fired coal plants is both technically and economically feasible at commercial scale. Further, the economic feasibility of reaching the sizeable national and world markets with such a modular device is enhanced by the US' recent extension and enhancement of the "45Q" tax credit scheme, conferring upon operators a \$50 /ton of captured and sequestered CO_2 and \$35 / ton of CO_2 for that used in enhanced oil recovery (EOR).

MPE believes that regardless of the entry pace and penetration (and expansion) into markets of renewable-sourced energy, existing coal- and lignite-fired facilities can remain productive and economically efficient for decades, and that provision of bolt-on capture capabilities to address any contemplated regulation scheme(s) will extend the useful life of adapted facilities for those decades. Corporate planers should not need to ignore or abandon lignite and coal resources for the near future.

In addition, the collateral value to other North Dakota markets (oil (via EOR, fracking advances involving CO₂), manufacturing, etc.) can be significant. In addition to discussion of this in the main body of this proposal, please also see Appendix 2 *Market Potential for the MPE Technology*.

The MPE team is qualified, experienced and prepared to demonstrate those feasibilities and opportunities, and to move toward scale-up and commercialization in this project.

Upon completion and analysis of the testing and operation of the test module a preliminary engineering effort will be initiated, to design a full size commercial module so that a feasibility-level cost can be completed. the engineering will include sizing of all equipment, preliminary system layout at a typical power plant, structural steel preliminary sizing, electrical one-line diagram and preliminary control system description will be completed. This effort will be initiated by the MPE design team and completed by a selected engineering group in a subsequent effort.

Equipment Purchases and Facilities: A unique aspect of this project is that MPE will provide a fully instrumented test system for assessing opportunities and methods for optimization of: steam and water utilization, vapor recompression costs, catalyst choice, lowering of the need for water re-vaporization, and improvements in the desorption step. Our

project collaborator, Great River Energy (GRE), will offer the use of its Spiritwood Station 99 MW lignite-fueled power generation to be the test site for the project, and GRE personnel will assist in conducting the test runs after receiving training to do so.

The primary technical focus of this proposal is to examine innovative approaches to heat integration and solvent chemistry that can reduce the cost and improve the efficiency of post combustion retrofit options for capturing CO₂ utilizing potassium carbonate from flue gas of existing lignite and coal power plants. Based on the results and previous work of Cousins et al. (2011ab), Koth and Araman et al., (2009), Nord et al., (2010), PFBCEET (2011), and RSE (2008), this proposal has several technical objectives, including:

- To collect experimental information from an unpressurized potassium carbonate CO₂ flue gas slipstream capture system to provide the basis for design of a full scale "bolt-on" additions to a lignite fueled power generation system at various capture rates;
- 2. To consider a generation/capture system as an entity, from fuel choice to utilization of the captured CO₂;
- 3. To evaluate the opportunities for more comprehensive heat integration within a system;
- 4. To reduce the reboiler duty and consider the use of mixed solvents in the adsorber / desorber system;
- 5. To reduce the capital / operating cost of capture (CAPEX, OPEX), while considering the lower depreciation costs for older power plants;
- 6. To reduce the parasitic load on the power plant and improve its overall efficiency. Each of these objectives is discussed in more detail in the work plan below,

Scope of Work

A key driver for business decisions about reducing the cost of CO_2 capture from lignite fueled power generation facilities will be the levelized cost of electricity costs per MWh. The approach is based on utilizing potassium carbonate and a combination of technical innovations, systems integration and a broader view of the overall economics. The project will involve utilization of an MPE test facility that has demonstrated the efficient and economical capture of CO_2 from pressurized combustion systems. The highly instrumented system can maintain safe operating conditions and it can easily incorporate modifications. For example, absorption of CO_2 into K_2CO_3 is an exothermic process and the energy released can be used to lower the reboiler duty in the desorption process. Other opportunities to be studied include: using mixed solvents in the absorption/desorption processes, applying advances in compression technology, use of plate heat exchanges and water as a heat transfer medium rather than steam. While the cost of CO_2 avoidance is the fundamental factor when considering post combustion capture retrofits, there are many other characteristics of both the plant and the site that may affect this decision and the choice of tasks to meet the desired objectives. Figure 1 illustrates how the choice of system boundaries influences the project scope and overall economics.

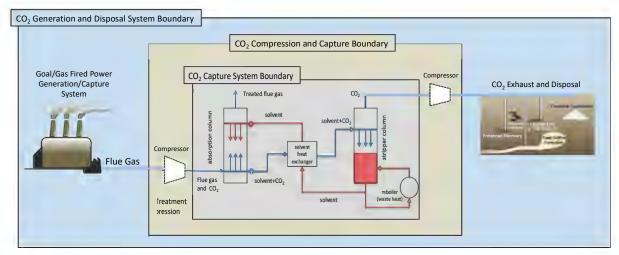


Figure 1 Different system boundaries for evaluating a CO₂ capture system

Some of factors that influence the overall economics are:

- 1. Characteristics of the power generation system (age, exhaust composition)
- 2. NO_x/SO_x and particulate controls at the site;
- 3. Restrictions caused by existing plant layout;
- 4. Proximity of the facility to a sequestration site;
- 5. Capture bypass provisions.
- 6. Market for the captured CO₂

Choice of Potassium Carbonate as the Technology of Choice

Carbon dioxide capture and storage (CCS) is an efficient way to reduce carbon dioxide emissions into the atmosphere and several methods have been considered. There are extensive literature reviews of such approaches including absorption, adsorption, membranes, cryogenic separation and combinations of these techniques. (see Hu et a. 2016; Chakma, 1997; Cowan *et al.*, 2011, Leung. 2014; Yu *et al.* 2012). Of these technologies, absorption is currently the closest to being commercially realized.

The absorption of carbon dioxide into an aqueous solvent was initially developed for purifying gases such as hydrogen gas, natural gas and synthesis gas. (Danckwerts and McNeil, 1967). Since then many solvents have been investigated for the absorption of CO₂, including monoethanolamine (MEA), diamines and tertiary amines such as piperazine and its derivatives (Bishnoi and Rochelle,) ammonia amino acid salts, ionic liquids, deep eutectic solvents MEA is regarded as the industry benchmark as it is the most widely used solvent. However, MEA has some disadvantages such as a high energy penalty for solvent regeneration, high degradation rate and corrosion.

Aqueous potassium carbonate is a good solvent for carbon dioxide capture because of its low regeneration energy, low degradation and low corrosivity (Bryngelsson and Westermark,

2009). The CO_2 absorption process using potassium carbonate solutions was first developed as the "Hot Potassium Carbonate (Benfield) Process". Potassium carbonate solutions have been widely used for synthesis gas purification. The CO2 capture system shown in Figure 1 has two key components, the absorber and desorber. The flue gas is fed into the absorber countercurrently to the solvent for absorption of CO_2 . The loaded solvent is then sent into a desorber, where CO_2 is stripped from the solvent by increasing the temperature or decreasing the pressure of the desorber. This desorbed CO_2 will then be compressed and liquefied for utilization or storage, and the regenerated solvent can be recycled back to the absorber for reuse in the absorption process.

The basic chemistry associated with CO₂ capture by potassium carbonate is the sequence of steps

$$CO_2(\mathsf{g}) \overset{1}{\longleftrightarrow} CO_2(\mathsf{aq})$$

$$CO_2(\mathsf{aq}) + OH^-(\mathsf{aq}) \overset{2}{\longleftrightarrow} HCO_3^-(\mathsf{aq}) \text{ (Fast)}$$

$$HCO_3^-(\mathsf{aq}) + OH^-(\mathsf{aq}) \overset{3}{\longleftrightarrow} CO_3^{2-}(\mathsf{aq}) + H_2O(\mathsf{aq}) \text{ (Instantaneous)}$$

$$CO_2(\mathsf{g}) + H_2O(\mathsf{aq}) \overset{4}{\longleftrightarrow} H_2CO_3(\mathsf{aq}) \text{ (Slow)}$$

$$H_2CO_3(\mathsf{aq}) + OH^-(\mathsf{aq}) \overset{5}{\longleftrightarrow} HCO_3^-(\mathsf{aq}) + H_2O(\mathsf{aq}) \text{ (Instantaneous)}$$

In the reaction scheme 1-5 CO₂ absorption is fast but not instantaneous. Typically the rate limiting step is (2) which in turn means a longer contact time is needed and as a consequence the absorber column can become quite large. Enhancing the mass transfer or the absorption kinetics are just two of the many ways in which the capture efficiency can be improved. Figure 2 shows many other options.

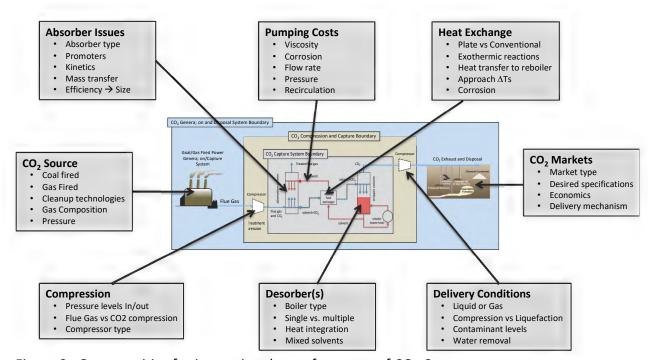


Figure 2 Opportunities for improving the performance of CO₂ Capture

The approach adopted in this study will be to focus on several critical aspects by exploiting opportunities for heat integration, solvent selection and compression cost. A key feature of the approach is evaluating the potential for improvements using a fully instrumented test rig.

Project Description

The project anticipates two phases, each representing approximately 50% of the allocated resources. The first, "Phase 1", will include inspection and modification of the test rig to be utilized at GRE's Spiritwood Station. The rig will be inspected (by a representative of its original design / manufacture team, plus MPE and GRE team members) at its current location outside of Pittsburgh, Pennsylvania. Necessary modifications (to render the rig compatible with atmospheric, or near-atmospheric pressure combustion systems) will be made, and the rig transported and installed with its control systems at Spiritwood Station. An initial set of tests and test runs to determine an initial capture efficacy will be done to conclude Phase I.

If the initial test runs confirm an appropriate operational platform, Phase 2 including the testing, scale-up design, financial and environmental analytical stages will be conducted, followed by a full, final report to the Industrial Commission.

Fourteen tasks constitute the group's approach to the project and the two planned Phases. They are sequenced in such a way so that the individual milestones provide a way to assess progress

Phase 1 EQUIPMENT MODIFICATION, DEPLOYMENT, PROCESS CONFIRMATION

Task 1. Inspection and modification of Test Rig

Following operation at the pressurized, fluidized bed combustion (PFBC) Vartan plant in Sweden the test rig was shipped to Pittsburgh, Pennsylvania (where it was installed and utilized at Consol Energy's Research Center) and used to capture CO₂. Testing at both the Swedish and US sites was successful and detailed reports of the performance are available. (see RSE (2008), Bryngelsson and Westermark (2009), and PFBEET (2011). Figure 1 shows the Test Rig in operation. Table 1 shows a summary of the gas composition and capture efficiencies achieved during the testing process in Sweden.



Figure 1 -- The Test Rig to be used (as installed at Consol Energy Research Center)

Table 1Gas Composition Before and After Pretreatment and CO₂ Capture Percentage

		After pre-treatment			After CO₂ capture		
Species	Inlet gas (by volume, wet)	Range	Average	Percentage Reduction by weight	Range	Average	Percentage reduction by weight
CO ₂	17 vol%	17.9-17.3	17.5	2.3	0.4-0.1	0.26	98.9
H ₂ O	13 vol%	11.9-6.5	8.7	N.A.	3.6-1.9	2.7	N.A.
N_2	67 vol%	73.2-67.0	70.6	N.A.	93.9-91.8	92.8	N.A.
O_2	<3 vol%	< 3.3-3.0	<3.2	N.A.	<4.2-4.1	4.2	N.A.
NO	17-27 ppm	17.8-10.8	15.0	28.6	15.5-8.9	12.0	56.7
NO ₂	0-7 ppm	N.D.	0	100	0	0	100
N_2O	37-51 ppm	47.6-36.4	40.6	1.61	66.2-41.4	54.3	-0.21
SO ₂	2-9 ppm	0-0.9	0.8	83.0	0	0	100
NH ₃	1-10 ppm	N.D.(<0.3)	0	100	0	0	100
HCl	10-35 ppm	N.D (<1)	0	100	0	0	100
HF	0-0.2 ppm	N.D (<1)	0	100	0	0	100
СО	0-9 ppm	3.8-3.7	3.8	-0.32	5.7-2.3	5.21	-4.01

The plant has served as a proof of concept installation, and has confirmed that: i) the pre-treatment of the flue gas is adequate for protecting the absorbent from degradation, ii) the CO_2 capture efficiency is high (> 98 %), iii) no harmful components are fed to the compressor, and iv) absorbent degradation is low (0.85 mole percent/month).

After completion of tests in Stockholm, Sweden, in Pittsburgh at Consol Energy's research center, and following Consol's unrelated, abandonment and sale of its research facility^{1,} the rig was recently placed into storage in suburban Pittsburgh. To achieve the performance required for the contemplated testing and experimentation, the rig will be thoroughly inspected to ensure, for example: 1) all the needed parts are serviced, or identified for easy replacement where pertinent; 2) that there has been no corrosion of any of the critical system (control system, absorber/desorber towers requiring correction; 3) the instrumentation is checked; 4) piping requiring internal cleaning is identified; and 5) a camera inspection of inside of pipes is done; and 6) ordering of parts to modify the system. A small crane and slings may be needed to lift and gain access to components to be inspected. A chemical cleaning will take place in North Dakota once the rig has been installed and pressure tested.

Deliverables: For these initial tasks, the original designer has been engaged to work with MPE team members to participate in the initial inspection to ensure that the rig is ready for transportation to the selected project site at Spiritwood Station, and further, is modified to utilize a minimal-pressure capture system at that location. The inspection protocol will be based on detailed flow sheet plans and parts lists. Attention will be given to identifying and ordering any replacement parts before the rig is shipped to the project location. The inspection and rig qualification before shipping will help minimize the technical and schedule risks. The project schedule will flex if necessary to accommodate "ordering and installation time" for necessary parts.

Milestones: Among sub-tasks and concepts planned to be undertaken or addressed at this point are: safety procedures on site, and other operational instruction and procedural discussion and provision of operator documentation to project participants.

Task 2. Project Initiation Meeting – Current Test Rig Location

Shortly after Task 1, or ideally concurrently, a meeting, including key project personnel will be held at the test rig storage location in Pittsburgh, to address and manage several detailed issues in preparation for the installation and operation of the test rig in North Dakota. Some of the specific items for discussion include:

- 2.1 Personnel management and information exchange between the parties about operational needs and the utilities needed to set up and prepare the plant for operation, (including installation of the utilities (power, water), etc.;
 - 2.2 Discussion of how slip stream flue gas will be connected to the test rig;
 - 2.3 Assessing the need, if any, for any preliminary gas stream clean-up;
- 2.4 Active safety and risk analysis and discussion for the site and its operation;

¹ MPE was asked to remove the test rig from Consol's facility due to Consol's selling of the entire multipleacre "campus" to a real estate developer unrelated to the energy industry.

- 2.5 Need for any short periods of 24-hour a day project-partnership shift support;
 - 2.6 Specifications associated with installing and operating a slip stream;
- 2.7 Instrumentation needs -- e.g. Fourier Transform Infrared Spectroscopy (FTIR) for characterization of composition of input and outputs from the test rig;
- 2.8 Characterization of flue gas composition under variable load;
- 2.9 Operation and plant access restrictions.

Conducting the meetings in Pittsburgh where the rig is currently stored will provide the opportunity for personnel to become familiar with assembly of the test rig, discuss installation procedures, and understand what will be needed to ensure successful installation and operation once the test rig is shipped to North Dakota.

Deliverables: A jointly prepared and approved document to address operational procedures, safety and security issues and identification that might be required for and MPE (or other) non-US citizen site entry. Ideally partnership personnel who will be involved with the installation/operation of the test rig once it is installed at the project site will attend this meeting.

Milestones: Inspection of test plant at storage location. Concerning test facility, conduct of status check; determination of new specifications for tests; order, or arrange fabrication re replacement or additional parts; order low-O₂ detection alarm; check and order sensors; check and order extra dosing pump; order gaskets (including spares); order flue gas re-compressor (for modest 0 - 3 atmosphere pressurization); final planning for erection of modules at test location.

Task 3. Project Initiation Meeting – North Dakota

At the outset of the project, a meeting will be held at the North Dakota site (Great River Energy's Spiritwood Station) to address several issues in preparation for the installation and operation of the test rig. The project team has extensive experience in working with power and chemical plant operations. Some of the specific tasks to be undertaken will include:

- 3.1 Staffing organizational specifics, training and information exchange between the two parties, including format of the final report;
- 3.2 Discussion of how slip stream flue gas will be connected to the test rig
- 3.3 Active safety and risk analysis for the site and its operation;
- 3.4 Specifications associated with installing and operating a slip stream from the power plant;
- 3.5 Characterization of flue gas composition under variable load;
- 3.6 Operation and plant access restrictions;

- 3.7 In addition to the site preparation issues there is also a need to assess the boundaries for the economic analyses, markets for CO₂ captured from a full-scale plant including EOR, sequestration, other chemicals.
- 3.8 Insurance and labor conditions coverage.
- 3.9 Instrumentation needs -- *e.g.* Fourier Transform Infrared Spectroscopy (FTIR) for characterization of composition of input and outputs from the test rig;
- 3.10 Need for any short periods of 24-hour a day project-partnership shift support;
- 3.11 Specifications associated with installing and operating a slip stream;

Deliverables: A jointly prepared and approved document to address operational procedures, safety and security issues and identification that might be required for and MPE (or other) non-US citizen site entry. Ideally partnership personnel who will be involved with the installation/operation of the test rig once it is installed at the project site will attend this meeting.

Milestones: Completion of each of the sub-tasks.

Task 4. Project Site Preparation before transport of the test rig

Given the rig dimensions and operating requirements determined from the previous tasks, project participants will need to prepare the connections to the needed utilities (electrical power, water, network access) as well as to the power plant slip stream itself. Ideally the slipstream needs to be taken after gas cleaning to remove, NO_x and SO_x , and particulates. The composition of the input to the test rig (CO_2 , H_2O , O_2) also needs to be characterized, should additional filters or gas cleaning need to be carried out. Detailed information about the composition of slip stream is to be evaluated.

Deliverables: Make certain, together with partnership personnel that the site preparation to receive the test rig has been carried out.

Task 5. Transport and Installation of test unit at North Dakota Site

After the initial inspection and the cleaning accomplished while the rig was disassembled, the task focus is the logistics of transporting the rig to the project site. A suitable transport company has been identified. What will be needed from partners is to provide of a suitable "lay-down" area outside the project area at which delivery and preliminary assembly tasks are to be done. A heavy-duty fork lift/crane will be required for unloading and placement of the test rig modules at the project site.

Once the required facility physical specifications (height, access, storage, analytical laboratory requirements, etc.) have been established as part of the project initiation, this task involves several important elements, including:

- 5.1 Site preparation to receive the test rig and inspection;
- 5.2 Organization of transport of the test rig to the site
- 5.3 Installation at the site

- 5.4 Operator training will be conducted and completed.
- 5.5 The next element of the task is to carry out a series of acceptance tests to ensure that all capture, control and instrumentation is working correctly to the required specifications.

Deliverable: Trained operators and a capture plant ready for detailed testing

Milestones: Test unit delivery and preparation of installment, erection and installment; delivery to and preparation of installment site; erection and connection of selected modules; installation of safe flue gas and CO_2 release piping; installation of O_2 alarm (closed building); controlled collection drain for absorbent spills; drainage for condensed steam and process water; auxiliaries hook-up and tests.

Task 6. Commissioning and Testing

Before carrying out detailed testing of CO₂ capture from the slipstream there are several critical steps that need to be performed:

- 6.1 Chemical cleaning of the piping systems,
- 6.2 Pressure testing of relief valves,
- 6.3 Integrity testing of control systems and instruments,
- 6.4 Loading of K₂CO₃ and water,
- 6.5 Start the system and record the slip stream composition.

The commissioning exercise will also serve as a way to initiate and test the Data Management Plan described in a separate section of this proposal.

Deliverables: In addition to reporting the results of the commissioning test a related activity will be the development of a process flowshweet model using AspenPuls/Hysys modeling system. This work will be carried out by researchers at Southern Illinois University and will build on the initial work carried out by Kothandaraman *et al.* (2009). The process flowsheet model will also serve as a way to carry out testing and sensitivity analyses to evaluate the likely impact of the proposed modifications to the test rig.

Task 7. Training of project partnership operators.

As a component of Task 6 a training course is planned to enable the GRE's assigned personnel to be able to operate the test rig independently of the MPE team. The training course will cover several topics

- 7.1 Safe operation,
- 7.2 Basic separation principles,
- 7.3 Underlying chemistry
- 7.4 Data analysis procedures.

During the experimental phase, there will be times when the test rig will have to be run full time for several days at a time to establish steady state conditions. This will involve shift operation and all the operators need to be able to understand how the test operates and what to do in the event of emergencies or out of specifications performance.

Deliverables: Training of personnel concerning testing regimes with safe operation of the test rig, including documentation of the commissioning processes.

Task 8. Testing and Analysis of Innovations using the Test Unit

MPE and GRE personnel will conduct initial test runs to confirm sufficient capture levels can be achieved to proceed with the full testing and design regime of Phase 2, moving toward at-scale commercialization.

Phase 2 Completion of Test Protocols, Evaluation and Analysis

By far the most critical task is the systematic evaluation of the alternatives identified for improving the performance of the potassium carbonate based capture system. In these tests, three innovations will be explored:

- 1. Operation of the system higher than atmospheric pressures,
- Solvent Selection and Heat Integration.

Each subtask is described in more detail below. These tasks are expected to entail: approximately 4 operators, including electro-mechanics and 1 supervisor, with the expectation occasionally to run in continuous overlapping shifts during test programs that may last from 1 to 2 weeks per tasks, with as a rule, no weekend shifts. Under no circumstances will any test be carried unless at least two or more people are present at all times. Call lists in the event of an emergency are to be maintained in prominent positions at all times. Health and Safety officials from the Southern University are to be involved through out the project duration.

Standard provisions for chemical storage and disposal are to in place at all times. In addition a disposal plan for equipment and chemicals at the end of the project are to be set in

place before operation of the test rig itself. Personnel access to the equipment will be controlled by locked entry to the building.

Task 9. Operation of the Carbonate System at Lower Pressure

Potassium carbonate is commonly used for CO₂ removal in industries and processes with a high pressure, e.g. in ammonia production. The Benfield process is one example of a commercial process that uses a 20 to 30 w% aqueous solution of potassium carbonate to capture CO₂. The slow rate of absorption, makes the conventional Benfield process unsuitable for coal fired power plants when used for post-capture at atmospheric pressure. Bryngelsson and Westermark, (2009) has identified the opportunity that comes from working with pressurized flue gas. The pressurized flue gas improves the equilibrium conditions and the operation temperature (about 100 C) improves the absorption rate. This task is directed at exploring the opportunity to run at up to 3 atmospheres (compared to the 10 bar levels used previously during the initial work with the test unit in Sweden and Pittsburgh) and higher temperatures with a goal to lower regeneration energy requirements as well as implement a highly integrated process that maximizes the heat integration between the power plant and the CO₂ capture system. Since the potassium carbonate is a much lower cost than amine based systems. K₂CO₃ is also non-volatile and non-toxic, which is an advantage compared to working with MEA that has many environmental trade-offs such as human toxicity and emissions of ethylene oxide during MEA production. The specific task involves:

- 9.1 Identifying the impact of pressure of the incoming flue gases and the need for compression above atmospheric. This will require the addition of a compressor/blower to the test rig so that the effects of increasing pressure can be codified. The compressor will be added during installation.
- 9.2 How the system performs at different power plant loads and desired capture levels
- 9.3 Estimating the heat of absorption and how waste heat from the power generation facility can be used to lower the reboiler duty.
- 9.4 Exploring the use of alternative solvents and enhanced mass transfer in the absorber/de-sorber columns.

These tasks are expected to entail: approximately 4 operators, including electromechanics and 1 supervisor, with the expectation occasionally to run in 2 overlapping shifts of ~ 14 hours during test programs of 1 to 2 weeks (10 days) each, with as a rule, no weekend-shifts.

Deliverables: Data on the CO₂ capture efficiencies at lower pressures, compression power consumption and opportunities for heat integration involving the power generation system will provide vital input to the economic analysis task.

Task 10. Solvent Selection and Reboiler Duty

A key determinant of the energy needed to operate the CO₂ capture system is the reboiler duty. The key objective of this task is to explore diverse ways to lower this duty by using a

dual boiler system that takes advantage of another solvent recirculation in parallel with the K_2CO_3 system. There are several desired properties of an ideal solvent for CO_2 capture including:

- 1. The solvent should contain a hard base, which will permit a strong affinity to CO₂
- 2. The solvent should have a solubility parameter (δ ') which is as close as possible to that of CO₂ under actual CO₂ capture process conditions
- 3. The solvent should be thermally and chemically stable to prevent degradation and formation of unwanted products under the capture process conditions.
- 4. The solvent should have a negligible vapor pressure (similar to that of ionic liquids) under the CO₂ capture process conditions in order to minimize solvent loss.
- 5. The solvent should have low viscosity under the actual capture process conditions to minimize pumping losses.

Table 2 shows a list of some of the current solvents in use that do not meet all of the criteria.

Table 2

hysical solvents used	l in commercial	nrocesses (Heintz	2011)

Process	Physical solvent		
Purisol ⁸	N-methyl-2-pyrrolidone		
Estasolvan	Tributyl-phosphate		
Fluor Solvent ¹⁵	Propylene carbonate		
Rectisol and IFPEXOL	Methanol		
Selexo, Sepasolv MPE, and Genosorb	Polyethylene glycol dialkyl ethers		

One other class of solvents that offers significant benefits as a way to reduce the re-boiler duty of a full-scale plant is the family of perfluorocarbons (PFCs). Perfluorinated liquids are extremely chemically and thermally stable, due to the high energy of C–F bond. The attractive properties of the perfluorocarbons (PFCs) that make them a potential alternative to current physical solvents are shown in Tables 3 and 4

Table 3Solubility of Gases in Perflurocarbons Heintz (2011)

	Gas solubility mL(gas)/100 g (solvent) at 25 °C and 1 atm									
Gas	Perfluoro- hexane	Perfluoro methyl- cyclohexane	1,3- dimethyl- cyclohexane	Perfluoro- decalin	Perfluoro- methyl decalin					
He	6.6	5.5	4.6	3.9	3.4					

H ₂	10.7	9.0	7.4	6.3	5.6
N_2	26.3	22.0	18.3	15.6	13.8
CO	26.3	24.2	20.0	17.1	15.0
O_2	41	34.6	28.6	24.4	22.0
CO ₂	156	132.0	109.0	93.0	82.0

- 1. As can be seen in Table 3 CO₂ displays much higher solubility in perfluorinated compounds than in the corresponding hydrocarbons, about twice as much;
- 2. Perfluorinated liquids vapor pressure is extremely low, and therefore solvent losses are minimum. (see Table 4)
- 3. Perfluorinated liquids have typically a relatively low viscosity, which could minimize the pumping and re-circulation costs of solvents; (see Table 4)
- 4. Perfluorinated liquids are non-toxic and completely safe under high pressure and temperature conditions.

Some of the drawbacks of perfluorinated liquids include, is their high cost. The approach to be explored in this task is to augment the reboiler with a light boiler that is loaded with the perfluorocarbon solvent. The task will involve some minimal alterations to the test rig to include a decanter and the light boiler. A key aspect will be to choose the boiling point of the solvent to reduce the overall desorber system heat duty.

Table 4
Physical properties of Selected Perflurocarbons from Flutec data sheets and Heintz (2011)

	PP10	PP11	PP25
Molecular Formula	C ₁₃ F ₂₂	C14F24	C ₁₇ F ₃₀
Main molecular species	Perfluoro - perhydrofluorene	Perfluoro- perhydro- phenanthrene	Perfluoro - (cyclohexyl methyldecalin)
Molecular Weight	574	624	774
Density (kg.m ⁻³)	1984	2030	2049
Boiling Point (°C) st 1 atm	194	215	260
Pour Point (°C)	-40	-20	-10
Viscosity (kinematic) (mm ² .s ⁻¹) at 25 C	4.84	14.0	56.1
Viscosity (dynamic) (mPa.s) at 25 C	9.58	28.4	114.5
Surface Tension (mN.m ⁻¹) at 25 C	19.7	19	-
Vapor Pressure (mbar)	<1	<1	<1

Heat of Vaporization at	71*	68*	67.9*
Boiling Point (kJ.kg ⁻¹)			
Specific Heat (kJ.kg ⁻¹ .°C ⁻¹)	0.92*	1.07*	0.957*
Critical Temperature (°C)	357.2*	377*	400.4*
Critical Pressure (bar)	16.2*	14.6*	11.34*
Critical volume (L.kg ⁻¹)	1.59*	1.58*	1.574*
Thermal Conductivity (mW.m ⁻¹ .°C ⁻¹)	56*	52.6*	63.8*
Coefficient of Expansion at 0°C	0.00078	0.00075	0.00084
Refractive Index n ²⁰ D	1.3289	1.3348	1.3376

In this task, two innovations will be explored: the specification of the solvent coupled with a way to reduce the mass transfer resistances that control the column height, and solvent recycle rates.

Deliverables Ranking of key process design variables and opportunities for full scale process optimization. The performance improvements are critical inputs to the economic analyses. The information collected from the test rig will provide a lot of data useful to the design of a fullscale capture system. A key output of this task will be an exploration of the use of a light boiler and perflurocarbon solvent to dramatically lower the reboiler duty.

Milestones: Proof of concept of the use of perflurocarbon solvent

Task 11. Reduce Pumping costs and Improving Heat Transfer

Cousins et al. (2011ab) and IEAGHG (2014ab) provide derailed reviews of alternative technologies for CO_2 capture. A recent paper by Lin and Rochelle (2017) suggest that one simple approach that can enhance the heat transfer between solvent and the re-circulated flow is the use of plate heat exchanges. They combine the advantages of lower approach temperatures, reduced pressure losses and higher heat transfer rates.

Deliverables: In addition to incorporating the plate exchanger there is also the possibility of using water as the heat transfer medium rather than steam in the reboiler. These performance improvements are critical inputs to the economic analyses. The information collected from the test rig will provide a lot of data useful to the design of a full-scale capture system.

Task 12. Analysis and adjustment of "going forward" levelized costs per MWh compared to the costs of low/no carbon alternatives.

The primary focus of this Task is to make a preliminary examination of the economics (CAPEX/OPEX) of the innovative approaches to heat integration and solvent chemistry that can reduce the cost and improve the efficiency of post combustion retrofit options for capturing CO_2 from existing coal and natural gas fired power plants.

While the cost of CO_2 avoidance is the fundamental factor when considering post combustion capture retrofits, there are many other characteristics of both the plant and the site that may affect this decision. For example, the additional space requirements for a full-scale plant with a CO_2 capture system and compression equipment. Bolt-on retrofits place additional demands on water for cooling and electrical power. Other factors that influence the overall economics are:

- NO_x/SO_x and particulate controls at the site;
- Restrictions caused by existing plant layout;
- Proximity of the facility to a sequestration site;
- Options for steam turbine modifications;
- Efficient use of condensate flow return;
- Capability to increase cooling systems;
- Capture bypass provisions.

The basic elements of the Task are:

- 11.1 Set the design basis as a power point plant size of 100 MW and lignite fuel type
- 11.2 Define the battery limits for the analysis
- 11.3 Establish the key parameters and their uncertainties e.g. fuel prices for coal and gas
- 11.4 Selection of the evaluation metrics from USDOE (2014), MIT (2009) and Hoffmann et al., (2001, 2004).

Ecology and Environment will participate with project partners to provide an overview of the environmental benefit of the project's findings and determinations with respect to existing and anticipated emission constraints, permitting and related effects for North Dakota and other anticipated commercial market areas.

Deliverables: An economic framework model for the evaluation of alternative process designs implemented in MS Excel; discussion of additional U.S. and world markets for

envisioned (next-phase) engineering and design of bolt-on system(s). Preparation of a component of the Final Report pertaining to the above. Environmental assessment / benefit summary. An assessment and discussion of environmental aspects of possible technology deployment across various regional and international regulatory schemes.

Task 13. Economic and Design Analysis of "Bolt-On" Solutions

Following confirmation of economically, environmentally beneficial CO₂ capture capability, MPE will conduct engineering and developmental activity toward a commercial, "bolt-on" system for application to existing generating facilities in North America and beyond.²

Dennis Williams will discuss design progress and issues; Tom Johns and Mike Mudd will focus on developmental issues and commercialization discussions with participants in pertinent markets. Ray Hattenbach will prepare and provide analysis of various beneficial uses of CO₂ (EOR, agricultural, automotive, fracking, etc.) at various capture rates and costs.

Task 14. Preparation of Final Report

The last task of the project will be the preparation of a final report and a submission of a journal article documenting the results of the project activities. In addition, during the project, periodic reports will be submitted to the contracting officer. The final report will include a high-level set of estimates of capital and operating costs for a commercial, bolt-on capture facility at various megawatt plant sizes.

Deliverables: A written final report, a MS Power Point presentation summary, and a draft of a Journal article to be submitted for publication after review by the project officer. Particular attention will be given to document the likely CAPEX/OPEX expenses and important technical and design issues associated with an implementation of "Bolt-On" solution for a full-scale plant.

Standards of Success

We expect to attain multiple standards to optimize development and commercial success for the project and the benefit of North Dakota, including:

 Achievement of successful, feasible results to lead to final commercialization work on near-atmospheric-pressure CO₂ capture from a coal- or lignite-fired power plant, as well as the determination of optimal technical and economic capture characteristics of tested chemistries at all pressure ranges. The project is expected to entail selection of primary economic target(s) for further pre-FEED work toward a scalable commercial bolt-on capture methodology suited to all existing lignite-fired generating facilities.

² Those to be installed in North Dakota will be offered by MPE (or by MPE-authorized manufacturers) on a royalty-free license basis to respective operating entities.

- Capture results enabling economic analysis of technology deployment achieving CO_2 capture rates from 60% ~90%.
- A favorable determination of such percentages at test scale, with extrapolations to at-scale projections;
- Determination of suitable economic projections for commercial deployment that support follow-on development efforts;
- Favorable results for possible North Dakota commercially beneficial uses of captured CO₂:
- Availability of collateral business interests (manufacturing base, etc.) with whom to offer further commercialization efforts;
- Identification of national and international markets for CO2 capture from existing coal and lignite;
- Establishment and stimulation of interest among North Dakota's manufacturing sectors to join in further commercialization efforts.

Accordingly, the phased project plan has been designed to contain internal deliverables, milestones communication processes and milestones to monitor and facilitate pursuit of the above.

The project involves the repurposed utilization of an MPE test facility that has demonstrated the efficient and economical capture of CO_2 from pressurized combustion – in terms of both capital and operating costs – and the MPE team anticipates that the proposed project activities will confirm a commercial opportunity to capture CO_2 at economically feasible lower pressures and suggest beneficial use of captured CO_2 in either EOR, fracking or other commercial areas.

Background

Mattoon Power Enterprises (MPE) is an energy development company that was formed as an outgrowth of Sargas, Inc., the US subsidiary of Norway's Sargas AS, for which a post-PFBC 3 CO $_2$ capture technology was developed by MPE team members Drs. McRae and De Meyer in the early 2000's. In connection with Sargas' 2016 restructuring, MPE has secured all pertinent rights to that technology 4 .

A sophisticated flue gas slipstream test unit, now owned by MPE, was constructed at a cost of approximately \$5 million to provide verification of the PFBC capture design (at

³ Pressurized fluidized bed combustion (PFBC).

⁴ More specifically, MPE was formed as a project development company for a pressurized 80MW coal generating facility at Mattoon, Illinois, on the site (which MPE has secured) of the original FutureGen location that had been selected in a national competition by then CEO, Michael Mudd, who is currently participating in this project. In the Qualification sections, management, project, technical and engineering personnel from the MPE team to be engaged in the proposed research are more fully described.

Stockholm, Sweden's Vartan PFBC plant, followed by further tests of the unit for pressurized systems at Consol Energy's Research Center, Pittsburgh).

As an example of a test report the MPE team will prepare, we have attached (at Appendix 10 the report of the test unit performance (under pressure), for the Vartan plant⁵ as prepared by Drs. McRae and de Meyer. We anticipate preparation of a similar account of test results for this project (in addition to the commercialization and design analyses discussed herein).

Since the pressurized tests in Europe and Pittsburgh, Drs. De Meyer and McRae have developed technical revisions and approaches for MPE to adapt its fundamental, greenfield potassium carbonate capture methodology into one that will suit and benefit existing, atmospheric generating facilities and provide environmental meaningful, and economically beneficial CO₂ capture results in order to design and produce a bolt-on system that can be marketed worldwide. The proposed testing and proposed scale-up design efforts are directed toward that end.

As described, this test unit will be moved to, modified for atmospheric and low-pressure testing and operation, and installed at Great River Energy's Spiritwood Station facility. There the unit will be used to conduct research to achieve commercially efficient capture under lower pressures. The test unit will be offered by MPE on favorable rental terms, with the substantially below-market amounts constituting a substantial part of the project's cost-share.

Because of its interest in efficient, economical CO₂ capture in connection with its generating activities, GRE has offered the space and utilities at its Spiritwood Station site location, as well as significant personnel resources for the conduct of project activities throughout the project period. These cost share elements are set out and discussed at *Cost Share Notes*, page 35

MPE estimates a 12-month project duration, beginning as soon as practical following grant-establishment matters and the practical constraints of North Dakota winters. Project initiation, followed by transport and installation of the test unit is projected for spring, 2018.In conjunction with the various milestones, processes and deliverables discussed under the pertinent task listings, the notional Gannt chart at *Appendix* 10 provides a guide to the anticipated progress over the period MPE projects.

Concerning interim reports, at the end of Phase 1, MPE anticipates providing a partial summary report to the North Dakota Industrial Council and the Lignite Research Council. Assuming a continuation to and through Phase 2, MPE will provide a summary report reflecting technical results, as well as analysis of economic and environmental commercialization matters, as well as impact on related North Dakota markets (manufacturing, EOR, etc.). Additional reports will be provided as may be requested and agreed during the project period.

We anticipate and plan compliance with the proposed dates upon which the interim reports required by section 43-03-05-8 will be submitted as will be agreed in the project contract.

⁵ The test and report involved Drs. McRae and de Meyer's work on behalf of the Norwegian entity, "Sargas AS", a company that has discontinued business, and from which MPE obtained the test unit.

The MPE team has previous large-scale project experience as described, most recently with the pre-FEED work done for its planned, greenfield, pressurized 80 MW facility to be located at land secured for that purpose at Mattoon, Illinois⁶.

Qualifications

In addition to personnel detailed from Great River Energy, set out below are the principal managers, researchers, and contracted project associates of MPE.

The team has extensive experience working together, in the design, testing, economic analysis, and operation of power generation systems and the regulatory environment for reduction of Green House Gases (GHG). More specifically, members of the project team were involved in the design, construction and operation of the test rig.



Paul D. Gandola will serve as principal investigator and project manager and will manage the efforts of the technical team -- with all of whom he has worked in a similar capacity in past years. Since 2008, Mr. Gandola served as the President of Sargas, Inc., a predecessor company to Mattoon Power Enterprises LLC, which was established in 2015, regarding the coal-fired greenfield project at the original FutureGen site at Mattoon, Illinois which he established with the economic development group at Mattoon, Coles Together⁷. Mr. Gandola is a lawyer and a member of the

Ohio and Pennsylvania bars, with experience in corporation law, both with the US Federal Trade Commission, and in private practice. He has extensive business development, consulting, entrepreneurial and project management experience, including management of technology-laden projects that have included NASA and US Air Force personnel and resources. Mr. Gandola holds a B.A. from Franklin and Marshall College, and a J.D. from Villanova University School of Law.



Gregory J. McRae is the Hoyt C. Hottel Professor of Chemical Engineering (Emeritus) at the Massachusetts Institute of Technology (MIT).

Dr. McRae is a co-author of two influential studies: The Future of Coal and The Future of Natural Gas (MIT 2007, 2009). These studies were carried out under the auspices of the MIT Energy Initiative, and were directed at developing policies for mitigating the impact of global climate change. In both reports he was responsible for the process technology

sections and testimony before the U.S. Congress. His teaching and research is related to the design and economic evaluation of environmentally benign process systems. He is the founder

⁶ This project is pending Illinois State Assembly action to redefine its "clean coal" standard to enable the necessary power purchase agreements within the State's existing clean energy goals.

 $^{^{7}}$ Angela Griffin is President of Coles Together, and was a collaborator in that project's organization and conduct.

of four companies that provide services to the microelectronics, combustion and chemical industries.

He received a M.S. and Ph.D. in engineering from the California Institute of Technology (Caltech) and a B.E. (Hons) in mechanical engineering from Monash University in Australia

Responsibilities: Dr. McRae's anticipated project activities will concern the overall deployment and administration of technical resources, testing processes and their results.



Herman de Meyer has 25 years of experience at Bayer Chemical Corporation (Germany) as Plant Manager and Senior Systems Engineer with company-wide responsibility for innovative chemistry and as a method developer introducing radically new process designs and improvements. He has been responsible for cutting-edge projects with capital costs exceeding hundreds of million dollars and introducing advanced engineering approaches. He holds numerous process patents.

Dr. de Meyer created his own company, Chemical Engineering Concept, and worked together with Prof. McRae of MIT, who arranged for Dr. De Meyer to be a visiting instructor at MIT. Their combined

experience in process design, industrial chemistry, control, operation and management allowed addressing and solving challenging process problems. Recently, in conjunction with the Norwegian company, Sargas, de Meyer produced several economically viable, compact and environmentally safe concepts (coal, lignite, gas) – including design work for the construction of MPE's initial-plant – which concepts have been evaluated with the focus on both commercialized applications and continued research to drive the "cost of CO₂ capture" even lower.

Dr. de Meyer holds a Ph.D. in Physical Chemistry from Leuven.

Responsibilities: In addition to Dr. de Meyer's contribution of new solvent and heat integration methodological concepts to the project in coordination with Dr. McRae's he will conduct on-site training, modification and operational initiation activities during on-site periods at both Pittsburgh and in North Dakota.



Dennis C. Williams, P.E. is to serve as principal engineering investigator involved with implementations of the proposed tests and to provide both technical and economic assessments the design elements of this project, toward a commercial, at-scale product. Williams has served for over 10 years as a Vice President for Business Development at SNC Lavalin's power division. As both an engineer and MBA, Williams provides MPE and the project with valuable engineering and commercialization resources, drawing not only on his SNC Lavalin experience, but on prior career management leadership positions at

Alberici Group, Tampella Power and Babcock and Wilcox.

Mr. Williams' academic degrees are from Brooklyn Polytechnic (B.S.) and the University of Virginia (MBA).

Responsibilities: Mr. Williams' responsibilities will involve, in Phase 1, supervision of engineering specification and application of modification components to adapt the test rig to atmospheric (and near-atmospheric) operation. In Phase 2, he will be involved in organizing the FEED tasks necessary to initiate design of a scaled-up, commercialized system. In addition, Mr. Williams will provide direct assistance to Dr. McRae in overseeing, reviewing and assessing test activities, with frequent on-site visits.



Michael J. Mudd, in addition to his work with MPE, is a recognized expert in clean coal technology, he was the Chief Executive Officer of the FutureGen Industrial Alliance which partnered with the US Department of Energy to build the world's first zero-emission power plant. Mike was R&D Manager at American Electric Power and has served on numerous committees including the US DOE Hydrogen Technical Advisory Council, the IEA Clean Coal Review Board, the Clean Coal Technology Coalition, the National Coal Council, the EPRI Gasification Experts Group, and the Technical Expert Review Committee for the Victoria and Australia

Governments.

Mr. Mudd's undergraduate degree was from Stevens Institute of Technology.

Responsibilities: Mr. Mudd's project role will concern assessing the commercialization market opportunities for the bolt on system(s) available, as well as assisting to identify engineering aspects for further design and commercialized system development.



Thomas A. Johns, Principal of Johns Consulting, LLC, has over 25 years' experience in power plant development and electric utilities. He has worked with MPE on past projects, managing development planning, project financing issues and modeling project economics. He specializes in development, permitting and financing of power projects and has experience in the development of coal, natural gas and renewables projects. Prior to his current role he was Vice President of Development for Summit Power, LLC, a developer of large-scale energy projects.

Mr. Johns received his Masters in Taxation from Gonzaga University and a BS in Accounting from Montana State University and is a CPA.

Responsibilities: Mr. Johns is assigned to assess project economics, financing issues related to bolt-on systems and the use and monetization of tax credits.



George A. Rusk, Vice President of Ecology & Environment Inc. (E&E) has over 25 years' experience in environmental law. He has worked with MPE on past projects, managing the environmental assessment component(s). He specializes in the review and analysis of Federal and State environmental legislation and regulations; obtaining permits and evaluating environmental impacts associated with coal mine development. He has extensive experience in project work in the United

States and overseas. Other responsibilities include coordination of matters involving regulatory agency proceedings; participation in legislative and adjudicative hearings; site assessments and regulatory compliance audits; negotiation with agencies regarding the scope of remedial programs.

Mr. Rusk received his law degree from the State University of New York at Buffalo and his undergraduate degree in Political Science from Yale University.

Responsibilities: Mr. Rusk will direct Ecology and Environment's environmental assessment (including implications fo commercialization) of the test results and the assessment of those results in terms of worldwide environmental "acceptance" of a bolt on unit per current and anticipated regulatory schemes.



Ray Hattenbach is currently President of Resource Development Consultants LLC providing consulting services to companies involved in Enhanced Oil Recovery using CO2 and in the development of natural gas liquids recovery using proprietary novel membrane technology. Prior to this he was Vice President of Engineering for Tabula Rasa Partners LLC, an independent oil & gas company that focused on the redevelopment of two legacy oil fields in the Permian Basin utilizing CO2. Concurrently, he was Vice President of Blue Strategies LLC which was formed in 2009 to develop carbon capture projects providing CO2 for enhanced oil recovery and geological

sequestration. Previously he had been Vice President of Business Development for Blue Source LLC, focused on the development carbon offsets from a variety of energy reduction and carbon capture and storage projects. He brings a wide range of business development experience in the areas of alternate energy development and chemicals with Phillips Petroleum Company and Dakota Gasification Company. His experience in energy resource development includes: enhanced oil recovery, construction of CO2 pipelines, geothermal drilling and production for power generation, uranium mining and milling, development of unconventional oil resources, coal gasification, Fischer Tropsch liquids and anhydrous ammonia from coal synthesis gas.

Since 2011 Hattenbach has served on the Technical Advisory Board for the U.S. Department of Energy's Plains CO2 Reduction Partnership which is directed by the Energy and Environmental Research Center and covers 3.6 million kilometers which includes all or parts of nine Midwestern states and four Canadian provinces. Ray served for five years on the Board of Directors of The Fertilizer Institute. He has a BS in Chemical Engineering from the University of Houston and a MBA from the Anderson School of Business, University of New Mexico.

Responsibilities: Mr. Hattenbach is assigned to assess the CO_2 technical and logistical realities of projected capture amounts and rates, including economics involving location utilization opportunities, pipeline capitalization, etc.



Paul D. Pansegrau is a Ph.D. chemist with numerous years of experience in fossil and renewable energy as well as the fine chemical and pharmaceutical industries. Paul was a participant in the commercialization of three products; the drugs Taxol® and Ifetroban® (Bristol-Myers Squibb), and Dimension® turf herbicide (Monsanto). Much

of Paul's energy career was spent with Dakota Gasification Company and the Energy and Environmental Research Center at the University of North Dakota. Recently, he retired from industrial employment to establish his own company, Technical Research Investigations LLC, and to join United Tribes Technical College in Bismarck as a chemistry instructor.

Paul recently attended the Second Annual Business Trip for Foreign Experts in Tai'an City, Shandong Province, China. Dr. Pansegrau received his B.Sc. (Chemistry) from the University of North Dakota; his Ph.D. in Organic Chemistry from Colorado State University, and he has done Post-Doctoral Research at The Ohio State University.

Responsibilities: Dr. Pansegrau will assist Drs. McRae and de Meyer with technical supervision at the North Dakota test site.

Value to North Dakota

This project will address several critical matters that corporate planners in the lignite, coal, power generation and distribution industries will deal with in coming years (and decades), considering various regulatory schemes and other market regulatory and economic realities. As discussed throughout this proposal, development of a commercially efficient means to efficiently capture and beneficially use CO₂ from existing generating facilities will:

- Sustain current sales of North Dakota's lignite and coal production, and facilitate opportunities for market growth;
- Preserve capital resources by extending the useful life of existing lignite- and coal-fired generating facilities;
- Maintain and extend employment opportunities at existing production and generating facilities across the affected industries;
- Assess additional economic benefits via various possibilities to use beneficially the CO₂ captured by the anticipated bolt on follow-on systems;
- Provide future research, design, manufacturing and marketing opportunities for North Dakota to create and deploy the "bolt-on" capture systems based on designs and methods the project will establish and confirm.

North Dakota, of course, has been actively supportive of the development and advance of carbon capture and management technologies, largely through efforts supported by the Lignite Energy Council. This project involves the same objectives -- designing efficient commercial scale capture of CO_2 with planned subsequent economic use of the captured CO_2 (for EOR, agricultural products, etc.).

To the extent this project yields an expected design and commercial availability of "bolt-on" CO_2 capture systems for existing generating facilities, the improved efficiency, regulatory compliance and lengthened life of those facilities, the availability of capital for purposes other

than rebuilding obsolete facilities, and the sustaining of current lignite markets will confer significant benefits to the State.

Concerning the specific priorities established in North Dakota Century Code section 54-17.5-03, MPE anticipates the project will satisfy and promote the necessary priorities. In addition, as specified in North Dakota Century Code section 43-03-02-02, the conforms to the following-described eligible projects:

"Any project proposing research, development, or marketing of lignite or products derived from lignite, or a land reclamation research project is eligible for a contract under this program. The following are examples of eligible topics: 1) Eligible lignite research projects include but are not limited to: ... c. Lignite desulfurization and emission control. ... f. Development of markets for liquids or other byproducts derived from lignite. ... h. Studies of legal, regulatory, and economic factors affecting lignite use and development. ... j. Development of commercial programs to treat effluent, emissions, solid waste, or hazardous waste from lignite conversion plants, chemical spills and oil spills, using bioremediation technology. k. Resource characterization and evaluation studies ... m. Development of advanced combustion systems, that is, systems with high efficiency and low emissions. n. In general, any project which will utilize or enhance the development or use of lignite resources."

Commercialization Opportunities

Existing Markets:

Within North Dakota and other communities with affected markets involving carbon capture considerations, the opportunity to attain a bolt-on technology for that purpose has presented a technical and commercial opportunity with self-evident benefits to the markets involved – lignite and coal production, power generation, oil production and agricultural products, with projected uses in "fracking" processes and others, as well.⁸

The United States, for economic (finance and operating) and regulatory reasons cannot efficiently build new non-CCS coal-fired power plants and is shuttering existing coal fired power plants. These existing coal-fired power plants retiring in the United States are among the cheapest source of electricity generation in this country. [emphasis added] To replace these plants with new generating capacity will cost the nation and thus taxpayers and consumers billions of dollars.

As contemplated, the MPE process involved in this project is expected to be "agnostic" in the sense that the specific method(s) of the existing plants' lignite or coal production methodologies are irrelevant to the envisioned ability of the bolt-on system to receive the resulting flue gas for CO₂ removal. As a post-combustion process, a bolt-on unit will simply require all flue gas to be passed to it.

Concerning existing markets, then, the preservation of lignite- and coal-fired units otherwise destined for shut down (for environmental, economic, regulatory or other corporate

 $^{^{8}\} http://instituteforenergyresearch.org/analysis/as-u-s-shutters-coal-plants-china-and-japan-are-building-them/$

planning needs) will provide significant market opportunities to <u>all</u> such existing facilities in the US, Europe, Asia and elsewhere.

Concerning the criticality of maintaining existing coal generating facilities, a recent DOE report⁹ emphasized the importance and resilience of coal fired plants to prevent regional shortfalls. Using the "polar vortex" of December 2017 / January 2018 as the example, DOE concludes "In PJM, the largest of the ISOs, coal provided the most resilient form of generation, due to available reserve capacity and on-site fuel availability, far exceeding all other sources (providing three times the incremental generation from natural gas and twelve times that from nuclear units); without available capacity from partially utilized coal units, PJM would have experienced shortfalls leading to interconnect-wide blackouts".

We expect commercialization instantiated by this project to lead to significant revenues from license and production of scaled-up systems, for which MPE will agree to provide negotiated shares to North Dakota's funding sources for this project, and in that regard will further encourage and support the development of North Dakota manufacturing participants. As the project progresses, we anticipate inviting members of the pertinent State manufacturing sectors to observe and work with MPE and the project toward these ends.

New-building of Lignite and Coal Plants

Some recent market-reported examples that present significant implications for major international markets imply a vast future commercial opportunity to integrate or "bolt-on" products that will result from this project's initiatives to such new systems:

China and Japan have plans to build massive numbers of coal-fired power plants, while the United States is not only not building new coal-fired power plants, but it is also shuttering many of its existing coal-fired power plants for several reasons. China is building one coal-fired power plant every 7 to 10 days, while Japan plans to build 43 coal-fired power projects to replace its shuttered nuclear units.

"In 2014, Japan issued its latest energy policy that emphasizes energy security, economic efficiency, and emissions reduction. Based on this policy, the country intends to develop the most advanced generation technologies using fossil fuels, strengthen the share of renewable and alternative energy sources, and reduce its dependency on oil in the transportation sector. Japan is the third largest oil consumer and net importer of crude oil and petroleum products in the world behind the United State and China.

"In that light, Japan is financing \$1 billion in loans for coal-fired plants in Indonesia and \$630 million in loans for coal-fired plants in India and Bangladesh. Japan is using climate finance funds for the projects since these new coal-fired plants are less polluting than older coal-fired plants and therefore qualify as clean energy. Japan believes that the promotion of highericiency coal-fired power plants is one of the "realistic, pragmatic and effective approaches" to deal with climate change.

⁹ DOE (NETL) report, "RELIABILITY, RESILIENCE AND THE ONCOMING WAVE OF RETIRING BASELOAD UNITS", March 13, 2018, DOE/NETL-2018/1883.

"China added 39 gigawatts of coal-fired capacity in 2014 — 3 gigawatts more than it added in 2013. That is equivalent to three 1,000 megawatt units every four weeks. At the peak, from 2005 through 2011, China added about two 600-megawatt coal plants a week, for 7 straight years. And, China is expected to add the equivalent of a new 600-megawatt plant every 10 days for the next 10 years. These new coal plants that China is constructing are more cleaner than their old coal-fired plants.

"China consumes more than 4 billion tons of coal each year, compared to less than 1 billion tons in the United States and 600 million tons in the European Union. China surpassed the United States to become the largest global carbon dioxide emitter in 2007, and it is on track to double annual U.S. carbon dioxide emissions by 2017. By 2040, China's coal power fleet is expected to be 50 percent larger than it is today and these power plants typically operate for 40 years or more¹⁰.

Commercialization design activity:

As the testing procedures and results begin to be known to the project, Dennis Williams will convene an MPE design group including Michael Mudd, Thomas Johns to consider matters pertaining to scaling up a system design to various commercial scale "targets", including not only chemical engineering and process factors, but mechanical engineering design parameters and construction implications, as well. Throughout the project from that initial point, the design group will monitor and update their planning (which will be included in MPE's final report) as appropriate.

If, as expected, the results of this preliminary engineering and feasibility cost estimate result in an acceptable cost of electricity projection for a utility sized facility, then more detailed engineering would be staged for a subsequent, next-phase of the project. Engineering at this phase would include firm equipment design and sizing. More detailed arrangement drawing of equipment and the necessary equipment list and piping information in order to develop a closer approximate cost for a full-sized module estimate will then be done.

Engineering at this level (typically at 20 -30 % of total required engineering effort for the final firm price costing) will include commodity quantities listed for estimating and data developed to get preliminary pricing for purchased equipment such as fans and pumps. A preliminary foundation design will be developed utilizing information from a pre-selected potential utility site or using typical soil data.

Final detailed engineering would be a much more extensive effort that will be deferred and developed in a subsequent phase of the commercialization process.

EOR opportunity analysis:

Ray Hattenbach will contribute his considerable CO_2 capture, CO_2 disposition and EOR experience (much within North Dakota and adjacent regions) to aspects of the project pertinent to integration the commercialization the CO_2 anticipated. This should be integral to meaningful

http://instituteforenergyresearch.org/analysis/as-u-s-shutters-coal-plants-china-and-japan-are-building-them/

pro formae that will be developed during the project to facilitate follow-on cooperation and funding from interested parties.

Tax Credits

Recent legislative developments that extend the "45Q" credits for a meaningful period are expected to affect positively all the pertinent commercialization economics. We expect to incorporate this element into the *pro formae* expected to be produced by Tom Johns in his capacity managing development issues.

Manufacturing Opportunities

MPE anticipates that a demonstrated capture efficiency for the technology will enable and facilitate the design and capitalization of a product that can be manufactured by existing and / or expanded precision machine facilites.in North Dakota.

A *pro forma* of the economics of the commercialized product will depend on further findings involving requirements for a full FEED (front end engineering and design), and the manufacturing systems and integrations required. Nonetheless, an example of EIA¹¹ cost data¹² concerning a generic flue gas desulfurization (FGD) equipment indicates the at-scale commercial opportunity a workable bolt-on unit will entail.

As the following EIA estimates indicate, we anticipate this system will represent close to \$50 - \$100 million per bolt-on system installation, depending on size, and we anticipate further that all manufacturing and integration processes can be provided by North Dakota industry. MPE will identify several North Dakota manufacturers with whom MPE expects to provide with requests for proposals for work involving integration and construction of the envisioned atscale, bolt-on capture system.

In the generic FGD case, EIA estimates an installed cost of \$288 / kilowatt hour of plant capacity. Extrapolating to a generic 400 MW coal-fired facility, the approximate projected cost of a bolt-on capture system is over \$100 million. Under the terms of this grant proposal, that indicates not only a significant manufacturing opportunity for the state, but, should any of the existing North Dakota generating facilities acquire and install the system, their royalty savings per year (at an assumed 2% rate), would be over \$2 million / year; at a 4% royalty rate, \$4 million / year savings. World Resources Institute identifies 1,200 coal plants in planning across 59 countries, with about three-quarters in China and India. A coal-burning power station in Beijing, China - the country is planning to build 363 new coal-fired power plants.¹³

MPE looks forward, as it assumes North Dakota will, to serving sizeable international market opportunities, about three-quarters in China and India.

¹¹ U.S. Energy Information Administration, https://www.eia.gov/.

¹² http://www.eia.gov/analysis/studies/powerplants/capitalcost

The recently enacted extension of the "45Q" tax credits will enhance the market opportunities for a bolt-on system; specific *pro formae* incorporating these credits will be developed during the project period.

From a capital cost point of view for the commercialized bolt-on product, given the significant sunk costs invested in generating facilities and in the additional costs (\$2 billion in state-of-the-art technology) attributable to environmental controls¹⁴, providing additional technical solutions to maintain these facilities in production (and in compliance with EPA), and other current and anticipated strict regulatory air quality standards or carbon tax schemes is of significant economic benefit to the State, its coal producers and plant owner / operators. Consumers, of course, will benefit from the avoidance of unnecessary capital costs due to this life extension.

On the other hand, if no solutions are found, from a lignite industry point of view, (and assuming a current North Dakota production rate of 30 million tons of Lignite per year at an average cost (February 16, 2017) of \$17.71 / ton), the commercial value at risk due to a decline in lignite use due to uncontrolled CO_2 emissions can be considered as up to \$531 million annually.

Management

The applicant team will work to execute the tasks and schedule indicated above at the overall direction of Mr. Gandola, with Drs. McRae and de Meyer working on site to install the test facility and train local operators from Great River Energy to help conduct the tasks detailed above.

Dennis Williams will supervise engineering activities pertinent to the installation and modification of the test unit, in addition to developing the economic and environmental analyses. Commercialization assessments will be made by Mike Mudd and Tom Johns; environmental assessments by Ecology and Environment at the direction of George Rusk. Ray Hattenbach will assess CO₂ beneficial use opportunities and methods. Tom Johns will be active during Phase 2 with commercialization / development activity, as discussed.

Toward these ends, Gandola and McRae will supervise and maintain conventional project management software to organize, execute and track tasks and results contemplated herein. MPE benefits from having a team (and project partners) familiar with, and used to sophisticated technologies, as well as complex project conception and execution.

Biographical information for the MPE team designated to this project can be found above, at *Qualifications*, page 24.

¹⁴ "Lignite-fired power plants have invested about \$2 billion in state-of-the-art technology to keep our air clean." This investment accounts for 20 to 30 percent of the cost of a power plant. https://lignite.com/what-is-lignite/benefits-of-lignite/

Timetable

MPE estimates a 12-month project duration, beginning as soon as practical following grant-establishment matters and the practical constraints of North Dakota winters. Project initiation, followed by transport and installation of the test unit is projected for spring, 2018. In conjunction with the various milestones, processes and deliverables discussed under the pertinent task listings, the table at *Appendix* 9 provides a guide to the anticipated progress over the period MPE projects.

Concerning interim reports, at the end of Phase 1, MPE anticipates providing a partial summary report to the North Dakota Industrial Council and the Lignite Research Council. Assuming a continuation to and through Phase 2, MPE will provide a summary report reflecting technical results, as well as analysis of economic and environmental commercialization matters, as well as impact on related North Dakota markets (manufacturing, EOR, etc.). Additional reports will be provided as may be requested and agreed during the project period.

We anticipate and plan compliance with the proposed dates upon which the interim reports required by section 43-03-05-8 will be submitted as will be agreed in the project contract.

A notional Gannt chart illustrating the anticipated tasks and progress of the project is set forth at *Appendix* 9 , *Timeline*, page 51.

Budget

MPE a has prepared detailed budget summarized below, with cost share summarized in the following section. Additional budget tables are shown at Appendix 10 page 52.

Cost Summary (prior to application of cost share):

SUMMARY OF BUDGETED COSTS (prior to cost share application)							
CATEGORY	Pi	nase 1	Phase 2	Total Costs	% of Project		
a. MPE Personnel		\$184,200	\$211,460	\$395,660	25.03%		
b. Fringe Benefits		\$0	\$0	\$0	0.00%		
c. Travel		\$11,925	\$33,100	\$45,025	2.85%		
d. Equipment		\$475,000	\$475,000	\$950,000	60.10%	rig rental market value (before application of cost share)	
e. Supplies		\$16,250	\$11,250	\$27,500	1.74%		
f. Contractual		\$23,500	\$23,500	\$47,000	2.97%		
g. Construction		\$38,115	\$7,500	\$45,615	2.89%		
h. Other Direct Costs		\$35,000	\$35,000	\$70,000	4.43%		
i. Indirect Charges		\$0	\$0	\$0	0.00%		
Total Costs	\$	783,990	\$ 796,810	\$ 1,580,800	1		

Cost Share Notes

The accompanying tables shows both in-kind and cash contributions. In the case of MPE, one of its "in-kind" contributions comes from foregoing over 2/3 of the commercial rental value of the test unit; another contribution comes from the indicated discount of labor and associated personnel charges.

Specific comments follow:

Cash:

MPE will contribute a total cash amount of \$187,200, in periodic installments that will be specified in the project contract.

In kind:

The estimated fair market value of the test rig involved, based on its \$5 million + construction price is set at \$950,000.00. Using industry-based monthly rental rates (calculated as market value / 36 months) the resulting monthly rental value of the rig is \$79,166.67. MPE will offer an in-kind cost share of \$49,167 per month, as shown in the cost share table at Cost Share Notes, page 35. MPE anticipates discussion of specifics and any necessary adjustments will occur during the contract negotiation period.

Personnel costs are indicated per rate suggestions from GRE, and are shown, prior to inkind cost share contributions at \$200 base rate, to which we have applied (for GRE personnel) a 15% discount for personnel hourly charges.

Additional repayment of grant funds, North Dakota license-free use, and revenue sharing:

MPE will offer royalty-free licenses of the commercialized version to North Dakota-based generating facilities that use the produce. In addition, we will negotiate future MPE contributions to the State, based on received revenues that follow commercialization from pertinent market.

The following, and material at Appendix 10 *Additional Budget Details*, page 52, sets forth comprehensive budget projections for the project phases and items indicated.

The budget includes the indicated MPE cost share elements, plus (in addition to waiver of North Dakota royalty payments) additional value MPE has established as follows:

Foregone overhead charges:

We note that MPE has charged no overhead or indirect costs to the project. This has been done to provide even more "skin in the game" by MPE – beyond its indicated in-kind and cash cost shares, and to provide an constraint on total project cost and funds requested.

MPE's cash contribution is shown. MPE anticipates making its cash contribution proportionally in advance of each Phase, or invoicing period, as may be agreed. MPE has additionally discounted its personnel hourly charges, as shown, and has include a *gratis* component of hours directed toward organization of local commercial interest to manufacture the resulting bolt-on product.

GRE will forego and contribute all charges for professional labor and site-based resources, as indicated.

Cost Share			
Cost Share Item	Phase 1	Phase 2	Total Project Cost Share
arket value rent based on indicated rig value, es based on rig value / 36 month rental	\$295,000	\$295,000	\$590,000

	or in Kina)	cost				Cost Snare
MPE	In Kind	37%	foregone market value rent based on indicated rig value, monthly rates based on rig value / 36 month rental	\$295,000	\$295,000	\$590,000
MPE uncharged hours	In kind		Uncharged hours for commercialization networking	\$2,000	\$8,000	\$10,000
MPE cash	Cash	12%	periodic payments, periods to be agreed	\$93,600	\$93,600	\$187,200
Discount to hourly personnel charges	In Kind	3%	15%	\$21,870	\$21,870	\$43,740
GRE	in kind	3%	personnel	\$25,000	\$25,000	\$50,000
GRE	in kind	3%	facility and utilty cost contribution	\$25,000	\$25,000	\$50,000

		Iotais	\$462,470	\$468,470	\$930,940
Total Project Cost:	\$1,580,800	Cost Share Percent of			58.9%
		Total Project Cost			

Total Cost Share: \$930,940

Type (Cash % of total

Source

(Phase 1) \$321,520 (Phase 2) \$328,340

Budget Notes

Cash requested:

- 1. The proposal presents separately the amount of MPE personnel professional "travel" hours ¹⁵ to be provided "on-site", both at the North Dakota test location, as well for modifications and instruction at the initial Pittsburgh test unit storage location. The aggregated budgeted amount for 8 on-site visits by MPE personnel, includes two involving the those of, Dr. de Meyer and a representative of the Norwegian contractor responsible for the test unit's initial construction.
- 2. Per diem costs for travel days are shown.

\$649,860

- 3. Balance of MPE professional hours allocated to the project
- 4. The full market rental value for the test unit is shown
- 5. Anticipated modification costs, to adapt the unit to proposed test operations

These hours are budgeted for both MPE and Great River Energy professionals at \$200 / hour. Per diem lodging and meals for MPE personnel are budgeted at \$175 / day.

- 6. Resources from Great River Energy will involve the indicated professional resources priced at the same rate as MPE's, along with a market-based charge
- 7. Rental space and utilities at Spiritwood Station

Schedule

The projected time for the completion of the indicated project tasks is 12 months. An illustrative chart of task durations and sequencing is at Appendix 9 , page 51.

Appendix 1 Summary of Previous Experience using the Test Rig

This Appendix provides a brief summary of the operational use of the Test Rig on a coal fired PFBC power plant in Sweden at Värtan. Further details can be found in Appendix 11, page 55.

Figure 1 provides a schematic representation of the associated process flowsheet and each section is discussed in subsections.

Pretreatment

The purpose of the pre-treatment stages is to remove dust and to absorb acidic gases (sulphur oxides, nitrogen oxides, hydrochloric acid and hydrofluoric acid) in order to minimize irreversible reactions with the absorbent. The PFBC plant at Värtan has comparatively low concentrations of acidic components due to lime addition to the fluidized bed and NO_x removal by SNCR, but additional removal is still necessary. The first pre-treatment stage is mechanic filtration to remove remaining small particles of ash and dolomite. The average dust levels in the flue gas about 93 mg/m3 according to long term statistics but the actual levels may vary considerably. Two parallel filters with a 2 μ m metallic filter elements from Porvair are used and the captured particles are dislodged from the filter elements by periodic back-flushing with pressurized nitrogen.

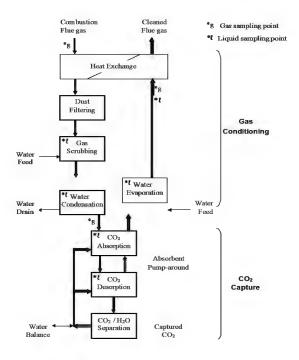


Figure 1.1 Functional process flow sheet for the existing CO₂ capture Test Rig

Pretreatment

The second pre-treatment stage is a co-current venturi scrubber, type LTB (LTB Lufttechnik Bayreuth GmbH &Co. KG). Fine water droplets are injected for saturation of the gas and removal of the fine particles that have passed the metallic filter. Some absorption of soluble gases is also expected. The water consumption for humidification was about 30 /h and the venturi water was recycled at up to 2m3/h with a pressure drop of maximum 0.6 bar. The third pre-treatment stage was a counter-current scrubber with a bed diameter of 0.20 m and a bed height of 2.0 m of structured packing of Mellapak 250Y. The water is recycled at a capacity of maximum 2.0 m3/ h and passed a heat exchanger for maximum 25 kW of cooling. Cooling of the water circuit is used for the condensation of vapour to reach water balance for the pre-treatment. Some additional absorption of microscopic particles and entrained droplets from the venturi may also be captured. Absorption of ammonia, hydrochloric acid and nitrogen dioxide is expected to be excellent since they are easily soluble in water. Carbon monoxide (CO) and dinitrogen oxide (N2O) have low solubility and are expected to be inert. Absorption of sulphur dioxide is dependent on pH value and may be improved by addition of alkali compounds like potassium carbonate. Absorption of al nitrogen dioxide (NO2) from the combustor was also achieved but nitrogen oxide (NO) was not.

Capture section

The purpose of the capture section is to absorb the CO₂ by a potassium carbonate solution, promoted with oxygen stable catalysts and corrosion inhibitors, and to regenerate the bicarbonate solution by steam. The CO₂ absorption column is designed for 95 % removal of CO₂ and the capture capacity is 13.6 kg CO₂/h. The column has an internal diameter of 0.2 m and has 4.0 m of structured packing of Mellapak 500X. The concentration of absorbent was 165gK/kg of liquid (equivalent to 29 weight % absorbent expressed as K₂CO₃). During the absorption cycle about 30 % of the K₂CO₃ is expected to react with CO₂ (after the absorption about 60 % of the K₂CO₃ is expected to be KHCO3 and after regeneration about 30 %). The regeneration column has an internal diameter of 0.3 m and contains 4.5 m of structured packing, Mellapak 500X. The heat exchanger for the regeneration has a maximum capacity of 50 kW. The condenser that partially condensates water from the regeneration gas is designed for 65 kW. The regenerated absorbent is cooled (up to 20 kW) before returning to the absorption column. The cooling compensates for the reaction heat during the CO₂ absorption that tends to heat the absorbent and evaporate water. The pre-cooling of the regenerated absorbent thus ensures a self-sufficient water balance for the capture section. The pre-cooler is also used during start-up. The outlet gas from the absorption is passed through an outlet scrubber (Di =0.2 m, packing height 2.0 m of Mellapak 250Y, maximum water flow 2000 l/h). Its purpose is to remove droplets of absorbents to minimize losses of potassium carbonate and a demister is used to capture the smallest droplets. In a complete plant the treated gas will be reheated to about 820°C by a heat exchanger and then led to the turbo expander. If the droplets are improperly removed they will get dried and produce a dust that may give some fouling of the heat exchanger and on the expander. If exposed to higher temperature than 891°C the potassium carbonate will melt and is likely to become much more corrosive, but the turbine used in Värtan has an operating temperature of about 850°C.

Sampling and analysis

Three flue gas sampling points are installed: 1) at the inlet to the pilot plant, 2) at the inlet to the CO₂ absorber, i.e. downstream of the pretreatment and 3) at the outlet from the pilot plant. The flue gas components CO₂, H2O, HCl, HF, SO2, SO3, NO, NO2, N2O, NH3 and CO were analyzed by an on-line FTIR instrument during measurement campaigns at steady-state conditions. The relative accuracy was 2 % and the detection limit (for wet gas), was 2.5 ppm for SO2, 1 ppm for HCl and

HF and 0.3 ppm for NH3. From the same sampling points physical gas samples were also taken. A sampling station with gas sampling cylinders was used for this purpose. Lab analysis of both gas and condensate collected in this way aimed at excluding the presence of specific trace impurities as well as droplets.

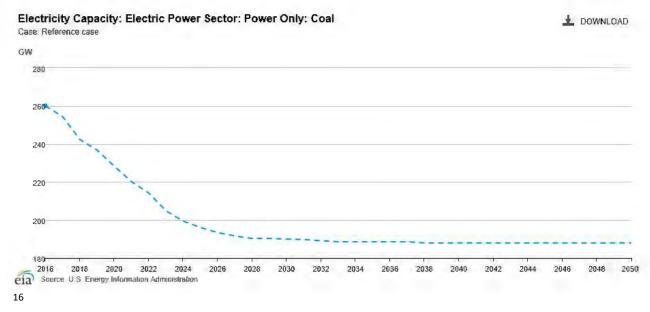
Six sampling points for liquid samples were installed: 1) recycle liquid from venturi scrubber, 2) from the recycle of the condensing scrubber, 3) rich absorbent from absorber, 4) lean absorbent from regenerator, 5) water from the recycle of the scrubber regenerator and 6) condensation water from cooling of cleaned flue gas. Gas and liquid sampling (for analysis in external labs) was carried out simultaneously. Liquid sampling for operational purposes and analysis by the operators in the Vartan lab was done on a regular basis during all shifts.

Operation

The pre-treatment was installed in May-June 2007 and successfully tested in June 2007 before the summer shutdown of the CHP plant. The rest of the pilot was installed during Aug-Sept 2007. The pilot was in operation during a total time of 320 h during Oct-Dec 2007. During the operation six (four in '07 and two in '08) different sessions were run with durations of 24-104 h each. The purpose of the different sessions was to verify that removal efficiency of >95 % can be obtained under different operating conditions (different flue gas flow rates, different recirculation rates and different degrees of saturation of the absorbent) and to verify good pre-treatment results for the flue gas during natural variations of the Värtan combustor (changed temperature, pressure, composition of flue gas). The flow rate of flue gas was measured and controlled automatically after the mechanic filter. The flow of absorbent was measured and controlled automatically after the regeneration and the temperature at the absorber inlet was adjusted by automatic control of the flow of cooling water. The flow rate of water recirculation in scrubbers was measured and controlled automatically, and their temperatures were controlled by control of cooling water flow. A SCADA system registered all sensor inputs in on-line data files, operator information (remarks, chemical analysis, actions taken, attention points, deviations, shift transfer information), specific instructions and details on the ongoing campaign have been accumulated in an electronic operator logbook.

Appendix 2 Market Potential for the MPE Technology

The 2018 Annual Energy Outlook (AEO) base cast forecasts a decline of over 52,000 MW of coal generation between 2018 and 2030. Most, if not all US utilities have removed future coal plants from their Integrated Resource Plans. A major factor of this projected decline is due to uncertainty about regulation of CO2 emissions, to the high capital and operating cost of Carbon Capture and Sequestration (CCS) technologies, and the projected abundance and low cost of natural gas. The AEO forecasts capacity additions almost 62,000 MW in the same time period. Within the projected capacity addition, AEO projects new 15,100 MW of new gas-fired combustion turbine combined cycle (CTCC) plants.



This projection could involve bad news for the potential market for coal plants in the United States, but actually the AEO forecasts point to significant market opportunities for new technologies that allow the efficient and cost-effective removal of emissions. Successful testing and commercialization of the Mattoon Power Enterprise system would be a paradigm change to the industry

Some specific consideration(s) of industry economic data. 17

The AEO projects the cost for a new Pulverized Coal Plant at \$3,453/kW without CCS, and \$5084/kW with CCS, or a cost penalty of \$1631/kW. The AEO projects the cost for a CTCC Plant at \$976/kW without CCS, and \$2227/kW with CCS, or a cost penalty of \$1251/kW. Until we have completed further testing, we do not have economic models to estimate the capital cost of installing our system into a new coal plant. However, the implicit simplicity of the system would intuitively be both capital and O&M costs.

¹⁶ https://www.eia.gov/outlooks/aeo/data/browser/#/?id=9-AEO2018&cases=ref2018&sourcekey=0

¹⁷ .All costs are in constant 2018 dollars.

The simplicity of the MPE system could lead to as much as a 50% reduction in the capital cost of installing a CCS system in a power plant.

If our system were to be retrofit into 25% of the coal plants slated to be retired, as a means to extend their lives, the market potential for that sector would be 13,000 MW, at a cost of \$625/kW, the market potential would be \$8.125 billion.

If the system were to be installed in 50% of the new capacity additions of CTCC plants, or 7750 MW, once again at a cost of \$625/kW, the market potential would be \$4.8 billion.

This outstanding market opportunity that would emerge upon the successful testing and demonstration of the MPE technology will benefit North Dakota in many ways. Demand for modular bolt-on systems should become the catalyst for the development or expansion of a significant amount of manufacturing facilities in the state. Further, during the negotiations for the grant agreement between MPE and North Dakota, in addition to royalty-free licenses to North Dakota generating adopters, we would be willing to work towards a mutually acceptable royalty sharing agreement for the balance of the market.

Appendix 3 MPE Mattoon, Illinois Project Summary

The following project summary has been prepared to describe the current state of MPE's Mattoon greenfield project, which has to date involved the following

Project Partners:









babcock&wilcox

- Mattoon Power Enterprises LLC Summit Power SNC Lavalin technology provider developer engineering
- Blue Strategies CO₂ logistics, Ecology & Environment Babcock & Wilcox oilfield management – environmental / permitting pressurized systems
- Michael Mudd project management (ex FutureGen CEO)
- Dr. Gregory McRae chief technology officer
- Dr. Herman de Meyer –technology officer

The Project – A New, Clean Illinois Coal-fired Power Plant + Enhanced Oil Recovery at Mattoon

- 400 acre site secured for:
- ~80 MW Coal-fired power generation at Mattoon's former FutureGen site -- expandable and:
- Utilizes proven, innovative, proprietary pressurized combustion technology to capture > 90% CO₂
- Will establish new Illinois industry with Enhanced Oil Recovery activity involving captured CO₂ and Illinois oilfields
- CO₂ sales offset power production and CO₂ capture costs power pricing under established rate cap
- Project financing and operation to benefit from 45Q credits

- Has completed initial engineering, environmental, costing and development tasks by world-class team
- Over 2 years of development with support from Illinois Department of Commerce and Economic Opportunity, Illinois Clean Coal Review Board, cost share from each team member
- Ready for FEED (final pre-construction engineering phase)
- Expected to secure private financing upon securing PPA via IPA and ICC actions

Appendix 4 MPE Cost Share / North Dakota Royalty Waiver / Letter of Commitment

MATTOON POWER ENTERPRISES LLC

March 26, 2018

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

Attn: Mike Holmes, Executive Director

Dear Mr. Holmes:

I am pleased to write, regarding the proposal material to which this letter is attached and confirm that Mattoon Power Enterprises (MPE) will make its CO2 capture test rig available and arrange to ship and install the rig facility at the specified North Dakota location GRE's Spiritwood Station made available for the project.

An in-kind cost share of \$590,000 of foregone equipment rental MPE is offering to this North Dakota project is based on a significant discount of a market-based market-related rental price of 1/36th of current equipment value as a monthly rental rate (exclusive of transport and installation costs) which MPE hereby offers and agrees to maintain for the 12-month+planned project period. In addition, MPE offers another \$10,000 of in kind, uncharged personnel time (specifically for anticipated networking with North Dakota manufacturing interests by MPE team members).

Further, we are pleased to offer a cash cost share of 5187,200 to the project.

Regarding the commercial-scale, bolt-on capture system we expect to design as a result of the conduct of this project, MPE intends to offer a royalty-free use license to any North Dakota entities that acquire and install a commercial-scale system. In addition, MPE intends to negotiate an agreement with the State to allocate a portion of the initial revenue stream from a commercial-scale system to repay the State within 3 – 5 years, for the grant amount awarded.

I will be happy to provide additional documentation and supplemental material upon request.

Best Regards,

Paul D. Gandola, President

1943 LORAIN BOAD - FAIRVTEW PARK - ORIO - 4425 - TEL: 440 - 725-0999 o mail: pgandola@n.netcom.com

Appendix 5 Affidavit re Tax Liability

MATTOON FUWER ENTERPRISES THE

STATE OF DILIO

AFFIDAVEL

Paul O, Candoln being first duly sound, states.

I am President of Matheon Power Enterprises LLC (MPE), and Ohio entity, and here alale that MPB, to the best of my knowledge, has no obstanting for his liability award to the State of North Daketa or say in its political subdivisions.

Paul D. Gerhands, President

Supern to before me, on this 23d day of March, 2017; at Fairview Park, Cayahoga County Ohio

Strikes N. Envell, Volary Tuble

My commussion has no expiration date.



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Appendix 6 Great River Energy Support Commitment



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tyurch 21, 2018

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

RL. Letterrof Support for Matteon Polassium Carbonate Based CD₂ Capture Project

Great River Energy believes that carbon capture and y theation may provide a pathway to maintaining the visibility of our base load lignife fired generating units in North Dakota under future carbon regulations.

Prior research has incicated that carbon capture and Sequestration is not energy intensive and costly to be practical anytime score. Mattoon's "bott on" technology has some interesting characteristics that may make it much less energy intensive and potentially more cost effective.

Creat River I nergy has agreed to collaborate with Matthon toward resting a pilot scale plant towalidate block characteristics. Great River Energy will provide the services of Charles Bollingen, as a co-Principal Investigator and determine specific plant modifications needed to facilitate the pilot test instrumentation required and establish the test protocols. Great River Energy will also provide approximately 2,400 so it of outdoor space at appriximately 6 the pilot scale plant along with labor, water and electrical utilities for the duration of the test valued at \$50,000.

Liteat River Energy will offer in-kind support estimated at \$100,000 (250 hours at \$200/hour +\$50,000 facilities).

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

Simberely,

CHEAT BIVE STREET

Sundry Brockerns
Director, Corporate and Pusiness Development.
(763) 446-5304

u

Mark Fagun Rick Lancaster

John Batter Charlle Bullinger

Paul Cardala, Marroni

Appendix 7 Basin Electric Support Letter



Geptomber 26, 2017

Mike Holmes Lignite Energy Council 1016 E. Owens Avenue Bismerck, ND 56502

Dear Mr. Holmes:

Ra: Letter of Support for Mattoon Power Enterprises CO₂ Capture

Basin Electric Power Cooperative (Basin Electric) is a regional, consumer-owned, generation and transmission cooperative formed in 1961 to supply supplemental power to a consoritum of rural electric distribution cooperatives. Basin Electric supplies 141 rural electric member cooperative systems with wholesale electric power who in turn serve approximately 3 million consumers in a nine-state area. Basin Electric's core business is generating and delivering electricity to wholesale customers, primarily to member systems.

Basin Electric considers CO₂ capture and utilization technology to be an important area of development to ensure the continued use of Lignite based power generation. However, additional research and development is needed to establish feesibility and improve the cost effectiveness prior to implementation at a large scale.

Mattoon Power Enterprises (Mattoon) is planning a pilot scale test at Great River Energy's Spiritwood Station, which utilizes Potassium Carbonale to capture CO₂ from North Dekota Lignite coal. Basin Electric has reviewed and discussed the project proposal by Mattoon, and is pleased to confirm its support.

It is Basin Electric's position that Mettoon's technology may result in improving the cost of CO₂ Capture, and that studying its effectiveness on North Dakota Lignite coal will provide value to the members of the Lignite Energy Council.

Sincerely.

Matthew Greek

Senior Vice President, Engineering and Construction

bh/lg

OC;

James Sheldon Benjamin Hertz Paul Gandola

Appendix 8 North American Coal Support Letter



General Auto

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March 20, 2018

Mr. Paul Gandola Mattoon Power Enterprises LLC 19443 Lorain Road Fairview Park, OH 44126

Re: Support of the proposed Post-Combustion Boll-On CO2 cepture test project as proposed by Matthon Power Enterprises

Dear Mr. Gandola:

This letter is intended to provide The North American Coal Corporation's (NACoal) support for Mattoon Power Enterprises (MPE) proposed Post-Combustion Bolt-On CO₂ capture test project.

NACoal is one of the top ten coal producers in the USA and operates coal mines in North Dakota, New Mexico, Texas, Louisiana, and Mississippi. In addition, NACoal is the largest dragfine operator in Florida, mining limestone.

NACoal is keenly interested in and closely involved with the development of new technologies and solutions to support the lightle industry. MPE's technology has the potential to provide NACoal's customers the ability to economically capture CO₂ from their time gas emissions.

We believe that, if successful, this project can significantly contribute to the continued development of the lightle industry in North Dakota, even in a carbon constrained world.

If you have questions and require additional information, please do not hesitate to contact me.

Regards

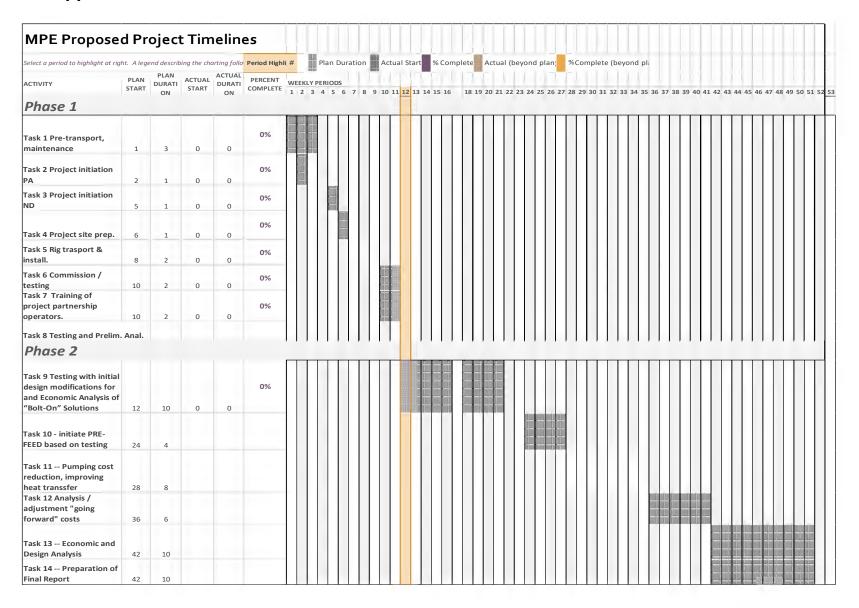
THE NORTH AMERICAN COAL CORPORATION

Dennis James

Director - New Technology

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Appendix 9 Timeline



Appendix 10 Additional Budget Details

Personnel									
Name, travel / local as indicated					Bou	Total	Project Total	Project Total	
mulcated	Time (Hrs)	Pay Rate (\$/Hr)	Total Budget Phase 1	Time (Hrs)	Pay Rate (\$/Hr)	Total Budget Phase 2	Hours	Dollars	
Name, travel / local	Hours	Rate (\$/hr.)	Total Phase 1	Hour s	Rate (\$/hr.)	Total Phase 2	Project Total Hours	Project Total Dollars	
Paul D. Gandola on travel	100		\$20,000					\$44,000	
Gandola local	80		\$16,000	60		\$12,000		\$28,000	
Gregory McRae on travel	60	7-00.00	\$12,000		V	. ,		\$28,000	
McRae local	80		\$16,000	120	\$200.00	\$24,000	200	\$40,000	
Herman de Meyer on travel	150	\$200.00	\$30,000	120	\$200.00	\$24,000	270	\$54,000	
Herman de Meyer local	58	\$200.00	\$11,600	96	\$200.00	\$19,200	154	\$30,800	
Michael Mudd local	40	\$200.00	\$8,000	60	\$200.00	\$12,000	100	\$20,000	
Thomas Johns	40	\$200.00	\$8,000	40	\$200.00	\$8,000	80	\$16,000	
Dennis Williams on travel	70	\$200.00	\$14,000	0	\$200.00	\$60	70	\$14,060	
Dennis Williams local	58	\$200.00	\$11,600	96	\$200.00	\$19,200	154	\$30,800	
Test unit designer - Norwegian	50	\$200.00	\$10,000	0	\$200.00	\$0	50	\$10,000	
Ray Hattenbach	0	\$200.00	\$0	75	\$200.00	\$15,000	75	\$15,000	
Paul Pansegrau	0	\$200.00	\$0	25	\$200.00	\$5,000	25	\$5,000	
Great River Energy personnel	125	\$200.00	\$25,000	125	\$200.00	\$25,000	250	\$50,000	
MPE uncharged hours	10	\$200.00	\$2,000	40	\$200.00	\$8,000	50	\$10,000	
Total Personnel Costs	921		\$184,200	1057		\$211,460	1,978	\$395,660	

3d Party Contractual

Vendor Name/Organization	Purpose and Basis of Cost	Phase 1	Phase 2	Project Total
Ecology and Environment	Envoronmental / Commercial Analysis and Report	\$12,500	\$12,500	\$25,000
Corrigan & Krause	Accounting	\$6,000	\$6,000	\$12,000
Insurance - tbd	Insurance	\$5,000	\$5,000	\$10,000
Total C	ontractual	\$23,500	\$23,500	\$47,000

Principal Equipment (prior to application of cost share)

	Months	Monthly Rate	Total Cost	Basis of Cost	Justification of need
Test Unit Rental (before cost share)- Phase 1	6	\$ 79,167	\$ 475,000	Market value (before cost share applied)	integral to / necessary for research proposed.
Phase 1 Total			\$ 475,000		
Test Unit Rental (before cost share) - Phase 2	6	\$ 79,167	\$ 475,000	Market value (before cost share applied)	integral to / necessary for research proposed.
Phase 2 Total			\$ 475,000		
PROJECT TOTAL			\$ 950,000		

Travel

	Depart From	Destination	No. of Days	No. of Flights	Per diem per Traveler	Each r/t Flight per Traveler	per	Tot. Per Diem Per Traveler	Cost per Trip
Domestic Travel			F	Phase 1					
Paul Gandola	CLE	PIT	10	0	\$ 175	\$0			\$1,750
Dr. Gregory McRae	CLT	PIT	6	1	\$ 175	\$700	\$0	\$1,050	\$1,750
Dennis Williams	CLT	PIT	7	1	\$ 175	\$700	\$0	\$1,225	\$1,925
International Travel									
Dr. Herman de Meyer	AMS	PIT	15	1	\$ 175	\$1,500	\$0	\$2,625	\$4,125
Design / build representative	OSL	PIT	5	1	\$ 175	\$1,500	\$0	\$875	\$2,375
Phase 1									\$11,925
Domestic Travel			F	Phase 2					
Paul Gandola	CLE	FAR	16	5		700	\$800	\$2,800	\$7,100
Dr. Gregory McRae	CLT	FAR	8	5	\$ 175	700	\$0	\$1,400	\$4,900
Dennis Williams	CLT	FAR	6	5	\$ 175	700	\$0	\$1,050	\$4,550
International Travel									
Dr. Herman de Meyer	AMS	FAR	22	3	\$ 175	\$1,500	\$0	\$3,850	\$16,550
Phase 2 Total									\$33,100
PROJECT TOTAL									\$45,025

Test Unit Transport-related

		Cost
Pre-transport modification of test unit		\$10,000
Transport and assembly of test unit, Spiritwood Station		\$38,115
Phase 1 Tota	I \$	38,115
Disassembly, out-shipment of test ujnit		\$7,500
Phase 2 Tota	I \$	7,500
PROJECT TOTAL	. \$	45,615

Appendix 11 Test report re pressurized tests at Vartan plant, Stockholm



Technical

Brasschaat, 19 February 2008

Finalized with new information & measurements

4 April 2008

Introduction

Capturing CO₂ from the pressurized flue gas of a coal fired plant is a novel technique pioneered by Sargas.

The Sargas process banks on CO_2 capture technology by absorption under pressure from a gas stream and desorption from a liquid absorbent of the CO_2 . This method is well established, is robust and has been in operation for years in the chemical industry. The kernel technology of the Sargas process, therefore, is the extensive flue gas conditioning before and after CO_2 capture.

The choice of pressurized fluidized bed combustion (PFBC) for coal is therefore a very natural one in the Sargas process as it has the advantage of "intrinsically" producing pressurized flue gas. The flue gas of the combustion produces electrical power (some 20% of the total) in a gas-turbine.

This poses specific constraints on the purity of the flue gas exiting the CO_2 capture subsystem on the one hand but, on the other hand, the flue gas conditioning required for CO_2 absorption (which is done before sending the cleaned flue gas to the gas turbine) is stringent to avoid loss of absorbent. The latter is an effective advantage for the turbine.

The Sargas DEMO plant at Fortum's site in Värtan-Stockholm serves as a proof-ofconcept installation.

The DEMO plant, therefore, was built and operated to demonstrate that the Sargas concept achieves the required flue gas conditioning, both to protect the absorbent and the gas turbine, in a robust manner.



Obviously, a major target for the DEMO plant is also to consistently prove, under different conditions, that the realized degree of CO_2 absorption is above the 95 %w goal. The DEMO plant is designed and equipped with the necessary sensors to allow different "experiments" (including different absorbent).

At the heart of the CO₂ capture plant is a well known absorption – desorption process using potassium carbonate as basic ingredient of the absorbent. As the basic principles this industrial process, in commercial use for over 60 years, are well understood (kinetics, diffusion, surface effects etc.), the design has actually been scaled down from an industrial chemical installation. The scale up of the installation is, therefore, not a problem. It is however planned that the most critical unit, the gas-gas heat exchanger, will be tested separately to ensure its scalability.

To allow the reader a better understanding of the technical issues discussed in this report, a simplified functional description of the capture plant is included as Figure 1. For ease of reference, the liquid and gas sampling points are indicated.



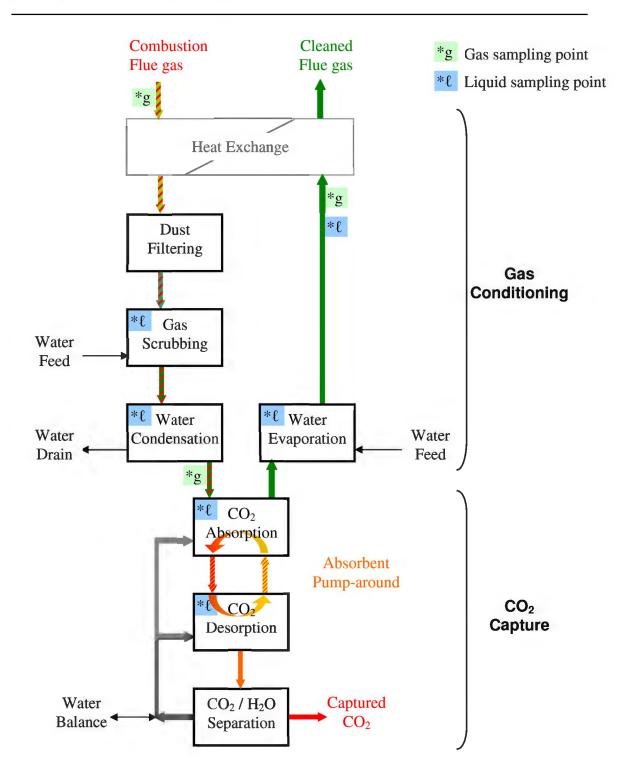


Figure 1. Functional description of the Sargas Värtan DEMO plant



The site of the DEMO plant in Värtan-Stockholm, gracefully made available and supported by the Fortum Research and Development department, imposed some obvious restrictions on the DEMO plant (in particular maximum flue gas flow and temperature). The gas-gas heat exchange part of the gas conditioning could, for that reason, not be installed. An illustrative plant description is given in Figure 2.

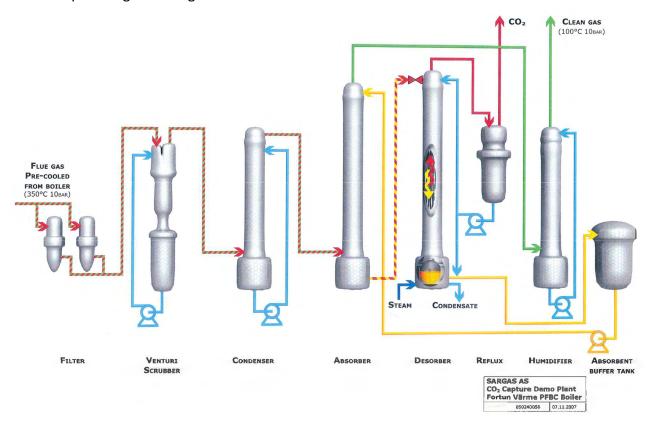


Figure 2. Graphical illustration of the Sargas Värtan Demo plant

Introduction to additional chemical analysis (February – March 2008)

During the 2007 campaigns only indirect evidence was gathered for:

- 1. The absence of vanadium in the cleaned gas
- 2. The purity of the produced CO₂

During the February and March 2008 campaigns direct evidence was provided, by analyzing gas samples, taken with 1 ℓ gas-bombs, directly from the lines carrying



Flue gas Cleaned gas

Both flue gas and cleaned gas were taken under pressure, at operational temperature and pressure (OTP).

The produced CO₂ was analyzed on-line for gaseous impurities during two campaigns. Nitrogen, argon and oxygen analysis were not planned at that time.

Missing error margins on boron and vanadium concentrations, relevant for the absorbent analysis, were provided by ALS Analytica.

A more appropriate carbon analysis was also used.

A more sensitive analysis method for chlorine was used to track chlorine traces.

All results are compounded in this document.

Safety & Environment

As safety and environmental issues are core concerns both for Sargas and Fortum, on whose premises the DEMO plant was hosted, maximum attention was given to both aspects of responsive care and considerable effort was invested.

While the CO₂ capture technology is new to the power industry and several "new" chemicals are introduced, robustness of the Sargas concept was also proven in this respect.

a. Safety

- i. A formal risk review was conducted (project team & Fortum experts)
- ii. All measures to reduce the identified risk factors were implemented
- iii. Some are counter-intuitive to the operators
- iv. Some safety requirements are implemented through procedures

b. Environmental

- Storage of chemicals in the plant was avoided by external preparation of the absorbent
- ii. ~ 1 kg absorbent has been "lost" into waste water capture containers
- iii. All operational samples have been recovered and treated



No accidents, spillages or major upsets occurred during operations.

Summary explanation of symbols and abbreviations used in the report

Several symbols and abbreviations that are obvious to persons with a technical background may not be obvious to readers that have different fields of expertise. A list of explanations is provided below.

PFBC pressurized fluidized bed combustion

%w percent by weight %m percent by moles %v percent by volume

ppmv parts-per-million by volume

wet adjective to a percentage or parts-per-million unit, it indicates that the

concentration was measurement without condensing water first

Fortum concentrations for CO₂ and impurity are reported as "dry"

OLLEMO reports all concentrations as "wet"

Concentrations on a wet basis are lower than when reported as dry

OTP shorthand for "at Operational Temperature and Pressure"; it is used to contrast

flow measurement or volumes to the their values obtained from sensors

calibrated for different conditions

UOP Universal Oil Products, a company belonging to the Honeywell group, which

holds the original Benfield CO₂ absorption patents (expired), having expertise in

potassium carbonate based absorption systems

Chemical symbols main components

CO₂ carbon dioxide

H₂O water

Chemical symbols gaseous "impurities"

NH₃ ammonia

NO, NO₂, N₂O nitrogen oxide, nitrogen dioxide and di-nitrogen oxide;

These components are commonly referred to as "NOx"



HCe hydrogen chloride
HF hydrogen fluoride
SO2 sulphur dioxide
CO carbon monoxide
Hg mercury

(K / V) ratio shorthand for the molar ratio of potassium (K) and vanadium (V); this ratio allows to detect entrainment of droplets. The Sargas absorbent used in the DEMO contains both of these elements in a specific ratio.

Summary of conclusions

1. DEMO goals

The Sargas Värtan DEMO plant has been conceived as a proof-of-concept installation with a number of goals.

At the same time, a number of possible goals were explicitly excluded, such as the heat balance, based on sound arguments. This determined the scope (and to a large extent also the budget) for the DEMO plant operation.

In summary, these are the major goals:

- 1. Capture of 95 %w CO₂
- 2. Show "adequate" cleaning of the flue gas
- 3. Gather process experience and data to support full scale design of flue gas cleaning & CO₂ capture
- 4. Judge "adequacy of cleaning" at entrance-of-turbine
- 5. Judge personnel impact Operation & maintenance

Laboratory & analytics

6. Judge transparency of procedures and automation / integration ability

All major goals were achieved; all technical goals are documented in this report.

The Sargas DEMO focuses on answering crucial questions regarding cleaning coal flue gas, with all its impurities, and producing turbine quality cleaned gas without traces of the absorbent. The integration of combustor and capture system itself could not be considered at the Fortum plant, mainly because of the limited size of the cleaned gas volume compared to the full flue-gas stream. Full scale CO₂ capture is now being evaluated in a separate project together with Fortum Värme.



As indicated earlier, new assessment of the energy requirements of the absorber/desorber capture plant was not included in the goals for Demo set up. The Sargas absorption-desorption system is well known in industry and industrial data are available and have been documented allowing derivation the effective energy levels involved in the process.

The "down-scaling" of the process would make it unnecessary cumbersome to generate data and they would in principle not add much new information. An important argument of a different nature is that the net energy requirement depends to a large extent on the plant configuration itself.

The DEMO plant is, purposely, not as sophisticated as the industrial design; simple extrapolations from the obtained heat balances would be futile.

2. On-line statistics

Scope, personnel and budget limitations as well as time pressure are an inherent ingredient of a small-scale installation.

- a. The plant ran 5 campaigns in 7 sessions
- b. Sessions with specific targets lasted 24 -106 h The average duration was 61 hours.
- c. The total number of hours logged during the 7 sessions is 360 h
 This excluded a number of short start / stop for testing, for procedure training or instrument failures
- d. The flue gas flow into the DEMO plant varied between 100 and 20 % with $9.3 \sim 1.6$ m³/h.
- e. The average gas load over the whole period is 6.2 m³/h OTP
- f. The CO₂ load has been varied 85 ~ 110 % of the design value.
- g. The total, integrated gas volume processed is 1210 m³ OTP

The concept proved intrinsically simple and robust.

3. Overall performance of the gas cleaning

All reactive impurities which are not captured by the gas cleaning system destroy the absorbent; non-reactive impurities may be co-absorbed with CO_2 and may cause quality loss in the CO_2 product.



- a. On purpose, no measures have been implemented to boost the gas cleaning (alkaline assisted scrubbing) during the campaigns ran so far.
- b. Reactive nitrogen impurities or for 18 %m found in the absorbent
- c. Chlorine impurities are NOT found to any significant level in the absorbent, only 0.85 %w of the processed HCl is recovered in the absorbent.
- d. Sulphur compounds or rejected from the cleaning and 50 %m is found in the absorbent
- e. "Loss of absorbent" due to impurities is, with 0.87 %m / month (chlorine accounts for only 0.02 %m / month), lower than industrial chemical practice

(e.g. 4 %m / month is quoted by UOP)

f. Known countermeasures will be implemented at the next campaign to prevent **all** sulphur and chlorine from slipping into the absorbent.

Absorbent quality remains very good and is expected to improve further.

4. Efficiency of CO₂ capture

One of the major goals of the DEMO is proving that CO₂ capture from a coal plant at a high degree of capture (95 %) is feasible.

- a. Under all different test circumstances regarding absorbent strength, gas- and CO_2 load the captured CO_2 was systematically in the range: 98 $^{\sim}$ 99.5 %m
- b. Load variations were between 86 ~ 108.5 %w
- c. Variations in
 - i. Combustor pressure (~ 3 bar)
 - ii. Flue gas entrance temperature (~ 100 °C)
 - iii. CO₂ contents of the flue gas (~ 4 %v wet)
 - iv. Water contents of the flue gas (~ 3 %v wet)pose no problems in maintaining quality of clean gas, CO₂ and capture.

The Sargas concept can guarantee 95 %m CO₂ capture efficiency.

5. Gaseous impurity removal

The removal of the gaseous impurities is impressive

- a. NO₂, NH₃ and HF are completely removed by the gas cleaning
- b. HCl traces were found in the absorbent with enhanced methods (Feb 28 '08)



- c. NO is ~50 %m reduced in the exiting clean gas
 - i. ~17 %m reacts with the absorbent
 - ii. ~25 %m is removed in the scrubber
 - iii. ~ 50 %m passes through the CO₂ capture system
 - iv. ~ 8 %m is the balance closure error

Follow-up direct measurements show that NO is NOT found in the captured CO₂ (see below)

- d. SO₂
- i. Is removed to only ~50 %m in the gas cleaning
- ii. The residual ~ 50 %m reacts with the absorbent
- iii. To stop this effect, known countermeasures will be taken; they do not change the Sargas concept at all
- e. N₂O passes through the whole capture system;

N₂O is NOT passing into the captured CO₂

f. CO passes apparently through the cleaning and capture system

Concentrations and number of data are too small to formally exclude the fact that CO may pass partly into captured CO₂

Follow-up direct measurements show that CO is NOT found in the captured CO₂ (see below)

Flue gas born reactants are totally removed in the Sargas concept.

6. Gas cleaning apparatus assessment

It appears that both the scrubber and the condenser play a role in the removal of gaseous impurities from the flue gas. The removal is so efficient that the liquid becomes acidic. Even when no special measures are taken to keep them alkaline, the removal efficiency is impressive.

- a. The scrubber removes:
 - i. Essentially all NH₃
 - ii. 10 ~ 40 %m of the sulphur species
 - iii. 50 ~ 90 %m of the HCl
 - iv. 15 ~ 95 %m of the nitrogen species
- b. The scrubber operation is a handful, as exemplified by the variations in specific efficiency. Construction details and time-pressured sensor purchases lead to compromises with little process information
- c. The essential remedies have no consequences for the Sargas concept
- d. Acting as a countercurrent scrubber, the condenser complements and compensates the scrubber fluctuations



- i. Cleans all residual NH₃ from the gas
- ii. Removes 1 ~ 10 %m of the sulphur species
- iii. Absorbs the balance of the HCL
- iv. Reduces nitrogen species by a further 10 ~ 15 %m
- e. The above numbers, with variations, were confirmed at very different operating conditions.

The multi-step concept for the gas cleaning is flexible and very efficient.

7. Cleaned gas quality

Samples from the humidifier and clean gas condensate attest to the quality of the clean gas leaving the CO₂ capture system, but are merely indirect evidence.

- a. All impurity levels in the liquid are at the μ g/ ℓ level (e.g. 20 ~ 75 μ g/ ℓ K)
- b. The (K / V) ratio in the humidifier indicates that minute amounts of fine droplets of the absorbent may escape from the absorber.
 - Obviously, the bulk of these is caught in the humidifier
- c. The over-proportional presence of boron indicates that some boron is volatilized. The prime candidate is the boric acid species.
 - All possible reasons for this effect appear purely operational.
 - The boron phenomenon occurs because the DEMO plant is aimed at identifying its limits.
- d. Again, the countermeasures are trivial and do NOT invalidate the concept.
- e. The analysis of "artificial" condensate of the cleaned gas only produces qualitative results
 - i. The (K / V) ratio indicates that droplets are NOT entrained from the humidifier
 - ii. The vanadium contents is extremely low (~3 µg/ℓ V)
 - iii. The "high" boron concentrations confirm their gas-born origin
 - iv. Surprisingly low calcium contents indicates a very high rate of dust removal

As a follow-up, gas samples were directly taken from the clean gas line (28 Feb '08 campaign) and analyzed for vanadium.

These direct analyses of the clean gas confirm the indirect evidence from the humidifier data that no vanadium from the absorbent is entering the gas to the turbine.



- a. Four gas sample were taken in 4 intervals of 5 minutes, were left to cool and create condensate for 14 days; the condensate was analyzed
- b. The vanadium contents is extremely low with an averaged concentration of 0.45 $\mu g/m^3$ flue gas (OTP)
- c. These values are on the detection limit of the methods used
- d. The amounts of condensate found by ALS Analytica in the different gas-bombs and collected with gas chromatographic syringes of 200 & fit well with the calculated amounts expected as condensate. The quantities of condensate are not mentioned in the official report but were confirmed verbally with the technician.
- e. This confirmation of the condensate amounts precludes that the vanadium originates from droplets entrained from the humidifier.

The clean gas is "turbine-ready" and is much cleaner than actual flue gas. No new chemicals will be entering the system: no K, no V!

8. Vanadium in PFBC flue gas

Apart from the clean gas and in view of the relatively high vanadium contents in one condensate sample taken earlier, gas samples of the flue gas were analyzed as a follow-up during the 28 Feb '08 campaign.

- a. The condensate of the flue gas contained rust and dust and digestion was used to check for vanadium
- b. Because of the surprisingly high vanadium content of the condensate, the analysis was redone using 2 different methods both results were equal
- c. The flue gas condensate quantity of ~500 µℓ confirmed that no droplets were present in the gas during sampling
- d. The vanadium contents of the gas derived from the Analytica results is extremely high with 3.95 mg/m³ flue gas (OTP)
- e. Most of this vanadium must reside in the dust as no candidate gaseous vanadium species are chemically feasible
- f. A follow up in the Värtan plant by Fortum confirmed that the flue gas contains vanadium (in the dust): $\sim 20 \,\mu g \,V/m^3$ flue gas (OTP)
- g. The vanadium was traced back to the coal (\sim 105 mg V/kg) as a source resulting in dust containing \sim 115 mg V/kg
- h. The flue gas dust itself cannot account for the extremely high vanadium concentrations found in the flue gas condensate sample



The flue gas vanadium concentration in the Värtan plant is, at this time, 2 orders of magnitude higher than in the clean gas from the CO₂ capture system

9. Dust

Gaining a more intimate understanding of the dust issues is part of the planned future work.

The possibilities for analysis in the Sargas Värtan DEMO plant are limited. The data collected so far indicate (only 2 results)

- a. The scrubber does indeed take out the fine dust particles.
 The best quantitative estimate is ~ 10 %w of the total load, fitting the particle size distribution closely
- b. The "forced" condensate of the clean gas contains calcium only in $\mu g/\ell$ levels, indicating very low dust entrainment and deposits in the gas line
- c. Quite independent of the exact absolute levels captured in the scrubber recycle and the condensate, this indicates the excellent performance of the dust filters

The 3 stage gas cleaning concept: gas filters, scrubber, condenser proved very effective in removing virtually all dust particles $> 0.1 \mu m$.

10. Captured CO₂ quality

During the 2008 campaigns on line gas chromatographic analysis of the CO₂ product was done to assess its quality.

- a. Of all the identified gaseous impurities in the flue gas, none were found to be over the detection limit of 0.5~1 ppmv in the CO₂
- b. The assumption made earlier in the February report that ~8 %v of the NO in the flue gas could end up in the CO₂ proves to be wrong: NONE was found

The quality of the CO₂ is high and it contains no aggressive comounds from the flue gas.

11. Future work

Three main topics will form the backbone of future work:

- a. Assessing the design of the gas-gas heat exchanger
- b. Implementation of improved conditions for impurity removal in the scrubber



(working with an alkaline instead of acidic recycle)

c. Collecting longer-term statistics

Technical note: more elaborate argumentation regarding the energy balances

Pragmatic arguments against retaining verification of the energy requirements and the energy balance of the CO₂ capture as a goal for the Sargas DEMO plant can be found in the document: "Goals for the Värtan DEMO plant" of August 11, 2007

A more elaborate enumeration of the three main reasons that led to the exclusion is included in this document:

· Data availability.

The Sargas absorption-desorption system is well known in industry and industrial data are available and have been documented allowing derivation the effective energy levels involved in the process.

Large-scale European and American government sponsored experimental programs have been completed or in progress to derive the energy characteristics to quantify the detailed basic physicalchemical processes chemical, whose combinations determine the energy requirements for the industrial process.

Several recent university studies, including large sized ones with several MW power plant equivalent flue gas flow, have been performed. Among them masters and doctorate theses in renowned institutions such Massachusetts Institute of Technology, Colorado School of Mines, Texas University, Fachhochschule Heilbronn, Technical University Delft, Nagoya University and several others, who, even in their search for alternative catalysts, absorbents, techniques, processes etc. determine, document and use the Potassium Carbonate process as a base line reference.

• Sizing and budget of the DEMO plant.

The Sargas DEMO plants size is, for the practical reason that it uses flue gas from an existing and operating PFBC coal plant, determined by the available facilities (e.g. size of membrane penetrating pipes, size of the building...).

The resulting, rather reduced size of the DEMO plant does not affect, in principle, the possibility to generate energy consumption data. However, a number of practical considerations make such an effort very costly indeed. The over-proportional size of flanges, valves, pumps and even apparatus shields with respect to the gas flow and liquid recirculation handled and the size of the apparatus makes insulation difficult and relative heat losses large.



Slender, long columns with surface to volume ratio's not comparable to a full scale installations and long liquid and gas lines due to restrictions on the geometry imposed by the existing power plant environment add to the heat losses and make them too large and not quantifiable.

Heat integration is for both geometrical and budget reasons not realizable to any reasonable extend if not too costly in man-hours.

• Process configuration.

More so than the "intrinsic" energy parameters of the process, the process configuration determines the industrial heat requirements.

Details of heat sources and heat integration, single or multiple loop operation and choice of recycling pumps and process integration are dominant factors for the energy balance.

The energy consumption number handled for a plant with:

- i. 90 %m CO₂ removal
- ii. 30 %w K₂CO₃
- iii. 30%m saturation difference absorption-desorption
- iv. 12 bar gas pressure
- v. No heat integration
- vi. A single absorbent loop

Is ~2950 kJ/kg CO₂; this would be the upper limit for the Värtan DEMO

An industrial system, with a more realistic configuration estimate for the capture system (no CO_2 compression)

- i. Coal flue gas cleaning
- ii. 95 %m removal
- iii. 25 %w K₂CO₃
- iv. 30%m saturation difference absorption-desorption
- v. 12 bar gas pressure
- vi. Simple heat integration
- vii. Two heat exchanging absorbent loops
- viii. Water recovery integration

Would be requiring 2180 kJ/kg CO₂

The balance between process integration and investment is, however very much dependent on local cost factors and configuration.



1. General conclusions

This report is based on the final reports of the chemical analysis of samples taken on November 15 2007 and December 13 2007.

The final reports of ALS Analytica (liquid phase) were available on January 17&23 '08. The final reports of OLLEMO (gas phase) were available on January 8&12 '08, they were corrected once more later on and distributed again on February 2 '08. Due to usually small differences between preliminary and final reporting of both independent partners, the results presented in this report may differ from those reported at the meeting in Stockholm on December 19, 2007.

a. Analytica reports

None of the Analytica reports refer to the original Sargas references and timestamps – as marked on the sample bottles. This attitude breaks the traceability chain required by ISO standards and makes it hard to track down anomalies.

All concentrations were reported on a volumetric basis without indication of the density or temperature. This leaves - especially for the carbonate solutions – a question mark as to the quantification as the density is a function of saturation, strength and temperature of the solution.

Reporting on a weight basis had been requested.

During the 2007 campaigns CO_2 could be detected in none of the samples of desorber and absorber and total CO_2 contents was systematically indicated as <1 mg/ ℓ for both.

This seemed strange for samples consisting of ~25 %w K_2CO_3 partly converted to KHCO₃ at levels up to 75 %m; such solutions contain up to 135 g/ ℓ CO₂!

For the 2008 campaigns the procedure for determining CO2 (as total carbon) has been changed and the total carbon content of the absorbent is now reported.

The method is clearly inadequate and leads to internally inconsistent reports indicating and error margin of an astounding \pm 80 %!

The consequence of this situation is that no "independent crosscheck" of the liquid phase results with the gas phase results can be performed (absorption and operation) on CO₂ capture and on the manual water balancing by the operators in the plant.

In spite of pre-order checks, the accuracy on the determination of the potassium concentrations in the absorber & desorber samples is far below expectations: the error margin appears to be \pm 12.5 %!

The potassium and carbon concentrations could be used in principle as a measure for the water contents in the absorbent and the fidelity of manual water-bookkeeping by the plant operators. The low accuracy of the analysis (K, B, V and CO_2) makes any independent cross-check futile.



This gross shortcoming, especially in combination with the loss of CO_2 distribution in the samples, also prohibits the correction and "rescaling" of the simplified analysis performed regularly by the operators to determine the CO_2 saturation in the absorbent (absorber & desorber). The latter is used to decide on operational changes in the plant. Some additional error margins on the measurement of concentrations in the absorbent were communicated.

- i. The error margin reported for boron concentrations is \pm 15 %! ii. The error margin indicated for vanadium concentrations is \pm 18 %!
- iii. These large margins on both boron and vanadium concentrations in the absorbent, even larger still than the margin for potassium concentrations, are useless to tighten the reconciliation on the absorbent parameters: strength and saturation
- iv. For sulphur components in the absorbent, expressed as mg/ℓ S, the error margin reported is ± 20 %!
- v. Error margins on the concentrations of other trace components in the absorbent originating from the flue gas and expressed as mg/l N and Cl (more sensitive method) are not communicated as yet. In short, the ALS results for desorber and absorber do not serve the purpose for which they were ordered. As will be commented on later, combined operator results and reported Analytica results are needed to make sense of all the absorbent samples. Although, within large margins, these data could be made useful but offer no "independent check" for the results and operation.

b. OLLEMO reports

Reliable measurements of the major components (CO_2 and H_2O) were made during all sampling sessions and properly documented. The results are in agreement with the online data from the Värtan installation.

Only during one single sampling period (15 Nov '07), all relevant "reactive" components – components that may react with the absorbent and destroy it such as HC ℓ , SO $_2$ and NO & NO $_2$ – were reliably measured. During this period liquid samples were also taken.

The incorrect (or absent) heating and insulation of sampling lines and the sampling cabinet, which creates condensates (NH₄C ℓ ...), invalidated a number of additional efforts by OLLEMO (28 Nov and 19 Dec '07). Gas components such as N₂O and CO, as well as NO to a certain extent, were measured during all sampling sessions.

c. Värtan on-line data



The availability of on-line analysis data from has been useful for obtaining trends for the operators.

Since the Värtan sampling is not situated at the combustor exit, but rather at the entrance of the stack, all had to be "interpreted" and corrected.

In the absence of complete OLLEMO data sets on the "reactive" gas components, Värtan data were used and combined with OLLEMO data to provide the interpretation of the removal of the reactive species in the gas cleaning and to estimate its performance from liquid desorber samples.

2. Overall assessment

With an overall assessment of the operational campaigns the safety, the operational functionality, the performance of the gas-cleaning section and the effectiveness of CO₂ capture of the plant is indicated.

a. For the purpose of this report, operational campaigns are meant to indicate prolonged periods of time in which the DEMO plant is continuously running at different operating points.

Relevant statistics will be reported on the basis of these campaigns only.

- b. This excludes the sessions in which the plant is purposely started and stopped (from and to several states of safety or operational readiness). Especially during October '07 these sessions have been held for several days for the purpose of operator training, interrupted frequently because of minor corrective actions on sensors, piping, insulation, computer configuration changes etc.
- c. Statistics, therefore, are based on the period of 9 Nov '07 5 Mar '08

Safety

Apart from 3 separate upsets with high pressure steam in which no damage or injuries were incurred and which were all under control within seconds, no "incidents" occurred.

All steam connections were revised and adhere to Fortum standards. Safety precautions, proper escape route and exit indications, emergency procedures, first aid kits and posted emergency phone numbers and instruction safety were available and at all times adhered to. No escape or leaks of the absorbent occurred.



On stream time and operation

The plant ran 5 campaigns in 7 sessions with durations of 24 -106 h; the average over 5 sessions being 61 hours.

The total number of hours logged during the indicated period is 360 h.

Availability of operators and shift leaders (in 24 hour regime) has been one of the constraints.

The gas flow taken into the DEMO plant from the combustor (4) has been varied between 9.3 and 1.6 m³/h at operational temperature and pressure; this represents a range between 100 and 20 % of nominal gas load.

The average gas load over the whole period is $6.2~\text{m}^3/\text{h}$ OTP and with the CO_2 contents of the feed gas being between 15.8 and 17.6 %v wet, this represents a CO_2 load of 85 $^{\sim}$ 110 % of the design value.

At the very lowest gas loads tested, $1.0^{\sim}1.5 \text{ m}^3/\text{h}$ OTP, the installation is no longer capable to keep the design operating temperatures in the cleaning section due to over proportional heat losses, in spite of countermeasures.

The total, integrated volume of gas processed during the period is 2210 m³ OTP.

Performance of gas cleaning

The focus of this section will be to review the chemical analysis of the impurities in the absorbent. The aim is to prove the effectiveness of the gas cleaning by showing which impurities are absent from successive sections of the plant. The complementing part of this analysis, showing where the impurities are caught (see liquid phase chemical analysis results) and how much passes through the system (see gas phase analysis results), will be presented later. Gas phase reactions may enhance the absorption of rather "inert" species:

g NH₃ + ½ CO₂
$$\rightarrow$$
 NH₂COOH g NH₃ + HC ℓ \rightarrow (NH₄)C ℓ g NO
+ ½ O₂ \rightarrow NO₂ g 2 NO₂ \longleftrightarrow N₂O₄ g NO + NO₂ \longleftrightarrow N₂O₃



g
$$N_2O_3 + H_2O \leftrightarrow 2 HNO_2$$

Water (scrubber, condenser) may absorb certain species and ionize them, whereby the equilibrium for the first five species and nitrous acid is driven the gas phase by the "strong" acids, which is essentially HC\mathcal{e} in the DEMO plant:

As the absorbent is a potassium carbonate based solution, any reactive component that enters the absorber with the gas may destroy some of it:

The destruction of the carbonate, as indicated by the reactions, leaves traces in the form of salts that accumulate over time and are traceable in the absorbent. Apart from decreasing the amount of active component in the absorbent they will also increase the risk of crystallization by the formation of rather insoluble double-salts.



In the scrubber (and in the condenser to a lesser extend) we can expect acidic conditions if the calcium carbonate, in fact excess dolomite from the combustor, is not sufficient to neutralize the acids present in the flue gas in reactions such as:

$$CaCO_3 + 2 HC\ell \rightarrow CaC\ell_2 + CO_2$$

If the gas cleaning is performing well, the absence of the above mentioned potassium salts in the absorbent may be taken as a good indicator for the efficiency.

Accumulation in the absorbent will continue as long as the absorbent is not replaced. The latter has not been the case in the DEMO plant.

As a basis of the evaluation, the measured average concentrations of the gas impurities together with the integrated amount of gas processed in the DEMO plant (since Nov 9 '07) have been combined.

The total amounts of each type of measured impurity that entered the plant and to which the absorbent has been exposed, are summarized in the table below:

Since all concentrations for HCl impurities were below detection limit during the 2007 campaigns no interpretation could be made. During the 2008 campaigns the plant has been exposed to more HCl impurities and, due to more sensitive analyses, concentration data became available.

The tables have been adapted to include these latest HCℓ results.

United Kingdom

Cumulative gas impurity feed (up to the indicated date)							
		15-Nov	13-Dec	Total*	15-Nov	13-Dec	Total*
Species	ppmv wet	g	g	g	g N-S-Cl	g N-S-Cl	g N-S-Cl
со	8.29						
N₂O	42.90						
NH ₃	5.17	6.48	26.84	35.19	5.33	22.07	28.94
HF	0.11						
NO	18.99	41.72	172.86	226.63	19.48	80.69	105.79
SO ₂	7.22	34.62	143.43	188.05	17.33	71.78	94.11
NO ₂	5.31	18.15	75.18	98.57	5.52	22.89	30.01
нс€*	31.22	84.17	348.75	502.91	81.85	339.11	489.01

^{*} HCl total results only are based on results from 28-Feb '08.

The results of the chemical analysis of samples from the absorbent are summarized in the following table: Accumulation of gas impurity in absorbent

	15-Nov	13-Dec	28-Feb*		15-Nov	13-Dec	28-Feb*
Element	mg/ℓ	mg/ℓ	mg/ℓ	Reacted	% input	% input	% input
N (tot)	33	121		N (tot)	25	17.4	
C€*	< 10	< 40	16	C6**	0	0	0.85
S**	< 800	265		S	0	50.8	
Absorbent	15-Nov	13-Dec	28-Feb	Load	15-Nov	13-Dec	28-Feb*



%w K ₂ CO ₃	28.33	33.69	22.67	g N (tot)	7.60	21.83	
%m KHCO₃	28.40	1.29	2.26	g Cℓ*	< 2.3	< 7.2	4.14
kg	308.9	249.0	332.1	g S	< 184	47.81	
ρ ²⁵ , kg/ℓ	1.342	1.380	1.281				
e	230.2	180.4	259				

^{*} HCl total results only are based on results from 28-Feb '08.

The gas cleaning takes more than 26.8%m of the Nitrogen impurities out of the gas, as will be further detailed in section 4; about 17.4 %m of the nitrogen ends up in the absorbent.

About 50 %m of the sulphur reacts with the absorbent but chlorine is stopped almost completely even under "acid scrubber operation"; the absorbent contains only 0.85 %m of the chlorine.

As will be shown in section 4 when discussing gas phase analysis, the absorption of acidic nitrogen and chlorine in the scrubber (and condenser) causes the respective recycled fluids in those apparatus to become slightly acidic. This causes the inefficient capture of SO_2 in the scrubber, but could easily be avoided.

Keeping the scrubber alkaline, e.g. by feeding a small bleed stream of K_2CO_3 or absorbent into it as was suggested by RSE earlier, may prove a valuable cure for this and is worth testing.

Apparently, the residual flue gas dust captured in the scrubber provides insufficient free Calcium carbonate to neutralize the Chloride captured. Nevertheless, a different alternative to provide alkalinity to the scrubber may consist in feeding small amounts of Dolomite into it.

The effect on the purity of the absorbent may be summarized – and put into perspective – as follows:

- The nitrogen compounds, found in the absorbent, amount to ~1.6 mol N. This
 would be equivalent to 1.6 mol of KNO₃, or a loss through reactions of 0.8 mol
 K₂CO₃
- The sulphur species amount to ~1.5 mol S.

This is equivalent to 1.5 mol of K₂SO₄, or 1.5 mol of reacted K₂CO₃

• The total loss of 2.3 mol K_2CO_3 compares to an active absorbent load of 619.7 mol and represent some 0.37 %m

^{**} Based on long term data provided by Fortum; details are explained in section 4.



- As this loss has been incurred over 320 h. Extrapolated to a month, the loss would be 5.25 moles or 0.85 %m.
- Chlorine causes very little loss of absorbent as the amount of it is only
 0.11 mol; this represents a loss of 0.01 %m of K₂CO₃.
- Even without alkaline assisted capture. this loss is significantly less than the 4 %m / month quoted by industrial providers (such as UOP) for the chemical industry!

Effectiveness of CO₂ capture

A lot of information is required to correctly calculate the mass percentage CO₂ captured by the system.

Synchronous data from the DEMO plant process computer to determine the flue gas feed from the combustor entering the plant comprise:

- Flue gas flow (as read from the flow meter)
- Flue gas temperature
- Flue gas pressure

To evaluate the water contents in the clean gas after the CO₂ capture and conditioning one requires:

- Clean gas temperature at humidifier
- Clean gas pressure at humidifier

To find the total CO₂ entering the system, which is the reference for establishing the capture percentage, data from gas analysis establishing:

Flue gas CO₂ and water contents of the flue gas

Unfortunately, these data are not available on the Värtan plant computers, while the sampling and analyses by Fortum have been conceived to check emissions to the stack. Since this stream is mixed with additional gaseous streams and air from ventilation systems and the like, its composition is not representative for the combustor flue gas.

To determine the residual flow of CO₂ leaving the capture system with the cleaned gas, one also needs to determine:

Clean gas CO₂ and water contents



The tables below show the relevant data for the measurement sessions

Item	15 Nov '0	7		
Input Värtan plant	Symbol	Value	Units	Remarks
CO ₂ in flue gas	CO _{2v}	15.83	%v	wet
H₂O in flue gas	H ₂ O _v	13.22	%v	wet
Input Sargas DEMO plant				
Flue gas flow	FIC001	5.93	m³/h	not OTP
Pressure gas in	PI001	9.47	barg	
Pressure gas out	PI006	9.15	barg	
Temperature gas in	TI001	228.8	°C	
Temperature gas to absorption	TI017	101.6	°C	
Temperature exit absorption	TI004	96	°C	
Temperature absorbent recycle	TI021	106.9	°C	
Temperature water recycle	TI022	60.3	°C	
Temperature exit humidifier	TI006	61.8	°C	
Saturation exit desorber	Slean	28.38	%m K₂CO₃	
Saturation exit absorber	Srich	35.41	%m K₂CO₃	
Absorbent strength	w	28.33	%w K₂CO₃	
Input clean gas analysis				
CO ₂ concentration in clean gas	CO ₂ clean	0.42	%v	wet



Item	13 Dec '07			
Input Värtan plant	Symbol	Value	Units	Remarks
CO ₂ in flue gas	CO _{2v}	17.0	%v	wet
H ₂ O in flue gas	H ₂ O _v	13.5	%v	wet
Input Sargas DEMO plant				
Flue gas flow	FIC001	5.56	m³/h	not OTP
Pressure gas in	PI001	9.48	barg	
Pressure gas out	PI006	8.32	barg	
Temperature gas in	TI001	198.8	°C	
Temperature gas to absorption	TI017	77.08	°C	
Temperature exit absorption	TI004	88.84	°C	
Temperature recycle	TI021	96.6	°C	
Temperature water recycle	TI022	37.23	°C	
Temperature exit humidifier	Т1006	65.77	°C	
Saturation exit desorber	Slean	1.26	%m K₂CO₃	
Saturation exit absorber	Srich	18.28	%m K₂CO₃	



Absorbent strength	W	29.78	%w K ₂ CO ₃	
Input clean gas analysis			24	
CO ₂ concentration in clean gas	CO ₂ clean	0.24	%v	wet

On the two following pages the results of the required calculations to establish the ${\rm CO_2}$ absorption percentage are summarized.



Derived output	15 Nov '07		
Item	Symbol	Value	Units
Fraction Inert flue gas	f ^v I	0.7095	-
Fraction CO₂ flue gas	f [∨] CO₂	0.1583	-
CO₂ flue gas - dry	CO _{2vd}	18.24	%v
Gas density @ Ρρ',Τρ'	$ ho_{\scriptscriptstyle G}$	6.149	kg/m³
Flue gas flow in	F _{flue} in	6.3	m³/h
Flue gas mass flow in	M_{flue} in	38.7	kg/h
Inert flow in	F _{Inertin}	4.47	m³/h
CO₂ flow flue gas	F _{CO2in}	1.00	m³/h
H₂O flow flue gas	F _{H2Oin}	0.83	m³/h
CO ₂ mass flow flue gas	M _{CO2} in	11.04	kg/h
CO ₂ mass absorbed	CO ₂ abs	10.86	kg/h
Pressure into absorber	Pabsin	10.31	bar
H₂O partial pressure into abs	p _{H2O} absin	1.072	bar
H₂O mass flow into abs	$M_{ ext{H2Oabsin}}$	3.82	kg/h
CO ₂ mass flow into abs	M _{CO2} absin	11.04	kg/h
Pressure exit absorber	Pabsout	10.23	bar



CO ₂ mass flow exit abs	M_{CO2} absout	0.18	kg/h
CO ₂ flow exit absorber	F_{CO2} absout	0.01	m³/h
H ₂ O partial pressure exit abs	p _{H2O} absout	0.737	bar
H₂O flow exit abs	$F_{H2Oabsout}$	0.26	m³/h
H ₂ O mass flow exit abs	$M_{H2Oabsout}$	0.66	kg/h
H₂O partial pressure condenser	p _{H2O} conout	0.202	bar
CO ₂ flow exit condenser	F _{CO2} conout	6.10	m³/h
H₂O flow exit condenser	F _{H2Oconout}	1.55	m³/h
H ₂ O vapor density condenser	$ ho_{\sf H2O}$ con	0.807	kg/m³
CO ₂ density exit humidifier	$ ho_{\sf CO2}$ hum	16.078	kg/m³
H₂O vapor density humidifier	$ ho_{\sf H2O}$ hum	6.624	kg/m³
Inert flow exit humidifier	F_{Inert} humout	2.86	m³/h
H ₂ O partial pressure humidifier	P H2Ohumout	0.202	bar

Derived output	13 Dec '07		
Item	Symbol	Value	Units
Fraction Inert flue gas	f ^v I	0.6950	-
Fraction CO ₂ flue gas	f ^v CO₂	0.1700	-
CO₂ flue gas - dry	CO _{2vd}	19.65	%v



Gas density @ Pρ',Τρ'	$ ho_{\scriptscriptstyle \mathrm{G}}$	6.182	kg/m³
Flue gas flow in	$F_{flue^{in}}$	6.6	m³/h
Flue gas mass flow in	M_{fluein}	40.4	kg/h
Inert flue gas in	$F_{Inertin}$	4.66	m³/h
CO ₂ flow flue gas	F _{CO2} in	1.04	m³/h
H ₂ O flow flue gas	F _{H2Oin}	0.87	m³/h
CO ₂ mass flow flue gas	M_{CO2^in}	11.51	kg/h
CO ₂ mass to be absorbed	CO ₂ abs	11.30	kg/h
Pressure into absorber	P_{absin}	10.31	bar
H ₂ O partial pressure into abs	P H2Oabsin	1.072	bar
H₂O mass flow into abs	M_{H2O} absin	3.98	kg/h
CO ₂ mass flow into abs	M_{CO2} absin	11.51	kg/h
Pressure exit absorber	P _{absout}	10.23	bar
CO ₂ mass flow exit abs	M_{CO2} absout	0.21	kg/h
CO ₂ flow exit absorber	$F_{CO2absout}$	0.01	m³/h
H₂O partial pressure exit abs	$p_{ ext{H2Oabsout}}$	0.737	bar
H₂O flow exit abs	$F_{H2Oabsout}$	0.27	m³/h
H ₂ O mass flow exit abs	$M_{ ext{H2Oabsout}}$	0.69	kg/h



H ₂ O partial pressure condenser	p _{H2O} conout	0.202	bar
CO ₂ flow exit condenser	F _{CO2} conout	6.35	m³/h
H ₂ O flow exit condenser	F _{H2O} conout	1.61	m³/h
H ₂ O vapor density condenser	р _{н2Осоп}	0.807	kg/m³
CO ₂ density exit humidifier	$ ho_{ extsf{CO2}}$ hum	16.078	kg/m³
H ₂ O vapor density humidifier	$ ho_{ ext{ t H2O}}$ hum	6.624	kg/m³
Inert flow exit humidifier	F _{Inert} humout	2.98	m³/h
H ₂ O partial pressure humidifier	p _{H2O} humout	0.217	bar

Additional data, from the campaigns in 2008, are also available.

Due to unfortunate circumstances, Värtan process computer information was no longer available. The evaluation for both campaigns ran so far, therefore, is based on average data over the measurement sessions to evaluate the capture efficiency.

The following table details the operation mode during the campaign when gas samples were taken for vanadium analysis.

Item	28 Feb '08				
Input Värtan plant	Symbol	Value	Units	Remarks	
CO ₂ in flue gas	CO _{2v}	16.60	%v	wet	
H₂O in flue gas	H ₂ O _v	13.30	%v	wet	
Input Sargas DEMO plant					
Flue gas flow	FIC001	7.64	m³/h	not OTP	



Pressure gas in	PI001	9.67	barg	
Pressure gas out	PI006	9.21	barg	
Temperature gas in	TI001	237.7	°C	
Temperature gas to absorption	TI017	94.8	°C	
Temperature exit absorption	TI004	86.8	°C	
Temperature absorbent recycle	TI021	92.2	°C	
Temperature water recycle	TI022	26.1	°C	
Temperature exit humidifier	TI006	69.4	°C	
Input clean gas analysis				
H₂O concentration in clean gas	H ₂ Oclean	2.8	%v	
CO ₂ concentration in clean gas	CO _{2clean}	0.30	%v	wet

Although the CO_2 load was high during this campaign, the resulting capture rate is insensitive to this parameter and is well above the target of 95 %m set for the capture plant design.



The relevant data during the March 5, 2008 campaign are summarized in the next table.

No liquid phase samples were taken during this campaign as it was dedicated to the confirmation of the CO₂ quality.

Item	05 Mar '08	3		
Input Värtan plant	Symbol	Value	Units	Remarks
CO ₂ in flue gas	CO _{2v}	16.50	%v	wet
H₂O in flue gas	H ₂ O _v	13.10	%v	wet
Input Sargas DEMO plant				
Flue gas flow	FIC001	6.31	m³/h	not OTP
Pressure gas in	PI001	10.02	barg	
Pressure gas out	PI006	9.59	barg	
Temperature gas in	TI001	216.6	°C	
Temperature gas to absorption	TI017	94.2	°C	
Temperature exit absorption	TI004	80.4	°C	
Temperature absorbent recycle	TI021	85.9	°C	
Temperature water recycle	TI022	27.9	°C	
Temperature exit humidifier	TI006	65.3	°C	
Input clean gas analysis				
H₂O concentration in clean gas	H ₂ Oclean	2.6	%v	
CO ₂ concentration in clean gas	CO ₂ clean	0.11	%v	wet

The CO_2 capture percentages following from these calculations are summarized in the following table. The last two entries in the table are the result of evaluations of data



obtained during sessions by OLLEMO in which only gasphase measurement were done. As indicated, the results are in line with the rest of the data.

Värtan DEM	CO ₂ load			
CO₂ capture	CO₂ capture %m			
15 Nov '07	98.19	86.0		
13 Dec '07	99.11	89.0		
28 Nov '07	98.73	108.5		
19 Dec '07	99.52	105.5		
28 Feb '08	98.78	110.8		
05 Mar '08	99.59	95.5		

3. Cross-check of absorbent concentration and saturation

In order to establish the CO₂ capture from the results of chemical analysis of the liquid phase, it is sufficient to know 3 items:

• The strength of the absorbent in the recycle loop between absorber and desorber.

The strength is merely the total contents of KHCO₃ and K₂CO₃ in the absorbent – but expressed as weight percentage K₂CO₃.

As all carbonate (or any non-volatile component in the absorbent for that matter) remains in the pump-around between absorber and desorber remains, the strength is also an indication of the water balance of the absorbent.

• The CO₂ saturation of the carbonate, which is the mol percentage of

K₂CO₃ converted to KHCO₃.

As CO_2 is absorbed into the absorbent, the saturation will increase. This also means that the total CO_2 contents per unit mass of absorbent increases. At the



same time, the ratio of total potassium to total carbon in the solution increases as well.

• The recycle rate of the absorbent.

This is one of the operators main control variable which is controlled and measured on-line.

Operators in the plant do not have the first two items, because the chemical analysis is too involved. A strongly simplified analysis is done and recorded, however.

It involves the determination of the total CO₂ content of absorbent samples taken from both the absorber and the desorber.

Given that the water balance of the capture system is carefully kept, the strength of the absorbent remains the same and the total CO_2 content is an indicator of the saturation and its trend.

This information is sufficient to run the plant.

However, the water balancing is to be done by manually compensating the difference between water condensed in the absorber from the flue gas and water evaporated from the absorber and water taken out of the water/CO₂ condenser/ separator with the CO2 on account of the partial pressure. Unfortunately, establishing the water difference has also to be done manually (spreadsheet) and any lapses, inaccuracies or skipped corrections will increase and cumulate errors.

As indicated earlier, the inaccuracy of the Analytica potassium analysis and the inability to correctly determine total CO_2 does not allow verification. The newly communicated error margins (March '08) on boron and vanadium do not help to improve this situation.

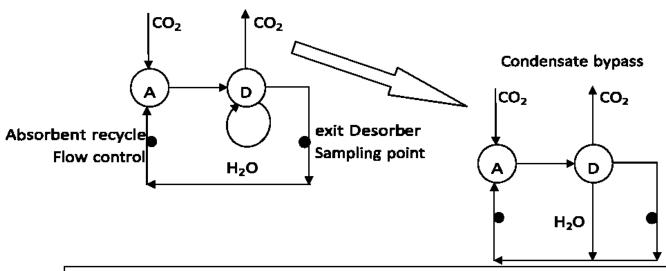
In order to make the data useful, a complicated scheme for data reconciliation of both incomplete and inaccurate results from the operators and Analytica was created.

The results, as far as they are real, show a large discrepancy between the operation as estimated from the operator analyses and the reconciled results.

For operation whereby the water condensate of the desorber bypasses the sampling point (as was the case from 13 Dec '07 onwards, see sketch) and water is injected directly into the recycled absorbent the Analytica data do not allow a close reconciliation, unfortunately. The reported concentrations of Boron and Vanadium are not feasible. "Using" the large error margin on the potassium allows a realistic result, but it proves that Analytica did not follow procedure and apparently filtered off a proportion of solidified carbonate and bicarbonate (no mention of it in their report), thereby concentrating both other major absorbent components.



The reconciliation was done by a specially developed "Gaussian" interpretation of the Maximum Likelihood method. The results are collected in the tables below:



Desc	orber	15 Nov '07						
Analytica	g/ℓ	±δ	% Best fit	g/ℓ				
K	231	29	12.6 K	219.9		W	28.3	%w
В	6.88		В	7.08		S	28.4	%m
V	7.73		V	7.52		ρ	1342	g/ℓ
CO ₂	< 0.001		CD₂	155.4				
Operator	6.22	g/sample	\rightarrow	6.21	g/sample			

Abso	rber	15 Nov '07							
Analytica	g/ℓ	±δ	%	Best fit	g/ℓ				
K	234	29	12.4	К	220.7		W	28.3	%w
				В	7.11		S	35.4	%m
				V	7.54		ρ	1347	g/ℓ
CO ₂	< 0.001			CO ₂	164.5				
Operator	6.58	g/sample		\rightarrow	6.58	g/sample			



Deso	rber	13 Dec '07							
Analytica	g/ℓ	±δ		% Best fi	t g/l				
К	273	34	12.5		269.1		W	38.2	%w %m
В	8.81		ı	 }	7.29		sρ	1.3	g/Ł
V	9.76		`	,	7.73		- 1	1380	G,
CO ₂	< 0.00)1	_		150.0	g/sample			
Operator	6.90	g/sample	· · · · · · · · · · · · · · · · · · ·	D ₂	6.00	g/sample			
							Wrecycle	29.78	%w
Abso	rber	13 Dec '07							
Analytica	g/ℓ	±δ	%	Best fit	g/ℓ				
K	209	26	12.4	К	232.8		W	29.8	%w
				В	7.13		S	18.3	%m
				V	7.57		ρ	1351	g/ℓ
CO ₂	< 0.00)1		CO ₂	151.6				
Operator	6.06	g/sample		\rightarrow	6.06	g/sample			

With only the accumulated manual accounting of the water and the total CO_2 analysis, the operators "best guess", is quite different from the above results. The operator information on total CO_2 , which was established at the same time as liquid and gas samples were taken, can be brought in quite good agreement with the Analytica results as is obvious from the above tables.

The explanation for the discrepancy between these two kinds of estimates is caused by the water balance and the errors in the follow-up on the Carbonate inventory; the latter changes continuously due to sampling. Cumulated errors and initial neglect to document and apply the balancing are responsible for this.

The water balance as calculated from the "best guess" estimates and the comparison with the operator's data from their laboratory measurements is illustrated in the table below.

From the discrepancies in the table and indeed from the discussion on the reconciliation and the combination on "partial and inaccurate" data, it may be hard to see where the "truth" is.



Possible explanations for the divergence may be found in the inaccuracy of the flue gas flow sensor FT001. It has been installed and re-installed in such a way that it has been vulnerable to dust and clogging (before filters) and after re-installation downstream from the filters it is situated too close to a sharp bend in the gas pipe, which may have caused "hysteresis" and too high readings.

In any case, one cannot rule out an overestimation of the flue gas input flow at this point. Fortunately, the results of the CO_2 capture are quite insensitive to such an error.

Estimate	Оре	erator	Reco	nciled
Date	15 Nov '07	13 Dec '07	15 Nov '07	13 Dec '07
Strength, %w	24.4	22.6	28.3	29.8
Water excess, kg	+8	+35	-41	-84
Abs Saturation, %m	67.5	68.1	35.1	18.3
Des Saturation, %m	56.7	58.7	28.4	1.3
ΔS, %m	10.8	9.4	7.1	17.0
Stock K ₂ CO ₃ , kg	87.5	83.6	87.5	83.6

The total carbon analysis from ALS Analytica, which was executed in 2008 with a "better" analysis method (all previous analyses gave 0 mg/ ℓ as a result!), should allow to:

Test the internal consistency of the absorbent analysis

Compare and rescale the operator measurements of the saturation

On February 27, 2008 at the start of the campaign, a sample of the absorbent was taken before the plant startup and sent to ALS Analytica for analysis determining of the "absolute" K_2CO_3 concentration of the absorbent. At the same time, an operator sample was also taken and analyzed to determine saturation.

It was hoped comparison of the results could be used to correct errors in the handaccounting of the water balance by adding or removing water from the absorbent.

The following tables contain the disappointing results of the reconciliation.

Absorbent	27 Feb '08	Reconciliation using the total CO ₂ result of Analytica



Analytica	g/ℓ	±δ	%	Best fit	g/ℓ				
К	227	28.2	12.4	К	187.8		W	25.3	%w
В	7.33	1.2	16	В	6.78		S	0.0	%m
V	8.04	1.4	18	V	7.19		ρ	1284	g/ℓ
CO ₂	69.6			CO ₂	103.4				
				\rightarrow	4.13	g/sample			

				1						
Absor	bent	27 Feb '08		Reconciliation using the total CO ₂ result of the operator					ator	
Analytica	g/€	±δ	%	Best fit	•	g/ℓ				
К	227	28.2	12.4	K		211.7		W	27.8	%w
В	7.33	1.2	16	В		6.94		S	0.0	%m
V	8.04	1.4	18	V		7.37		ρ	1315	g/ℓ
CO ₂	69.6			CO ₂		116.5				
Operator	4.66	g/sample			\rightarrow	4.66	g/sample			

If, as in the first table "Reconciliation using the total CO₂ result of Analytica", no realistic reconciliation results is possible. All concentrations of potassium, boron and vanadium are outside of their very large error margins.

If the reconciliation is done ignoring the Analytica results, but instead replacing them with the operator results all concentrations are within their error margins.

The Analytica CO₂ results are also not "internally" consistent, as shown in the table.

Internal consistency Analytica CO ₂ results	К	±δ	CO_2 required for species K_2CO_3	CO ₂ reported	CO₂ error margin
	g/ℓ	g/ℓ	g/ℓ	g/ℓ	%
K reported by Analytica	227	28	124.9	69.6	80
K at minimum range: - δ	199		109.5	69.6	57



For the Analytica CO₂ determination to fit:

- With the potassium (K) concentration as reported by Analytica one has to accept an error margin of 80 % for the CO₂ determination
- Even when one accepts the large error margin in the potassium concentration and replaces the "measured" K concentration by the value at its extreme minimum margin: $(227 \delta) = 199 \, \text{g K/\ell}$ has still has to accept an error margin of \pm 67 % in the CO₂ concentration.

This inaccuracy is unacceptable.

4. Gaseous impurity balance

In order to assess the balance of gaseous impurities and find out what the faith of these components are, one needs to derive the so called "shrinking factor" of the flue gas. As the flue gas passes through different stages of the capture process, as indicated in Figure 1, its temperature, pressure, its water and CO_2 contents may vary. The impurity levels may also change, but they are so small that their variation does not affect the flow of the flue gas. A correct assessment of the small concentration differences in the flue

gas occurring between the entrance and the exit of the CO2 capture system requires calculation of the extent of intrinsic volume loss (the shrinking factor) of the flue gas.

By dividing the measured concentration (e.g. expressed in ppmv) by the shrinking factor, one obtains the correct apparent concentration as if the species was "inert". This would imply that it does not react away during CO_2 capture and that it is not removed by the absorbent, in which case it would end up in the captured CO_2 stream.

In case no gas concentration measurements are available, this factor needs be estimated from operating temperatures, pressures and physical properties of the gas such as non-ideal behavior, partial pressure of water etc.

Referring to Figure 1 where the placement of all 3 gas sampling points is indicated, it is required to define two shrinking factors.

The first one, f_S^{absin}, allows comparison between gas concentrations at the entrance of the absorber and those at the plant entrance. It is useful to assess the effect of the gas cleaning itself.

The second one, f_S^{exit} , is required to compare gas concentrations between in- and outgoing gas and includes the effects of both the gas cleaning and the absorbent on the impurities.



In case measurements are available, as is the case in this report, the procedure is simple. The shrinking factors are derived from measured gas phase concentrations in the following way:

absin
$$100-\%vCO_{2absinwet}-\%vH_2O_{absinwet}$$

$$= 100-\%vCO_{2exitwet}-\%vH_2O_{exitwet}$$

$$f_{Sexit} = 100$$

 $100 - \% vCO - \% vCO_{2entrancewet} 2_{exit} wet - - \% vH\% vH_{22}OO_{entrance} wetwet$

Reviewing the data for all four periods for which gas phase measurements are available results in the following table:

Shrinking fact rs								
Date	Absorber entrance	Plant exit						
Nov 11 '07	0.984	0.727						
Nov 28 '07	0.940	0.728						
Dec 13 '07	0.919	0.718						
Dec 19 '07	0.940	0.717						

The shrinking factors can be used as follows:

Applying these factors (by diving by it) to the impurities concentrations observed in the gas entrance of the plant results in a concentration at the entrance of the absorber or for the plant exit gas respectively. These concentrations are to be expected if the specific impurity were "inert" to any influence of the capture process.

Comparison allows conclusions of whether the impurities:

Are captured in the cleaning section before absorption



React with the absorbent and destroy some of it

Dissolve in the absorbent and are released in the desorber with the CO₂

Pass through the whole system and remain in the clean gas (to the turbine)

The reported detection limits and accuracy of the gas analysis, as cited by OLLEMO, will have to be taken into account:

Compound	Accuracy
H_2O , CO_2	2 % relative
NO. NO2. N2O. CO	2 % "

 NH_3 2 % detection limit 0.3 ppm $HC\ell$ 3 % detection limit 1 ppm

SO₂ 2 % detection limit 2.5 ppm in wet gas

HF 4 % detection limit 1 ppm

The table summarizes the results and also presents the real, measured concentrations.

Gaseous imp	ourity c	oncen	tration	compa	rison (opmv we	et)	
Species	NO	NO ₂		N ₂ O NH ₃ HCl SO ₂ HF CO				
15 Nov '07	After gas cleaning							
Expected if "inert"	21.9	0.0	37.8	0.0	35.6	2.5	0.0	2.3
Measured	18.7		37.6		0	0		3.8
15 Nov '07	1'07 After CO₂ capture							
Expected if "inert"	30.2	0.0	52.3	0.0	49.2	3.5	0.0	3.2
Measured	14.7		56.6		0	0		3.7
28 Nov '07			Af	ter gas	cleanin	g		
Expected if "inert"	23.7	0.0	42.1	10.4	37.3	2.7	0.0	3.5
Measured	16.1		40.8	0	0	0		3.7
28 Nov '07			Af	ter CO ₂	captur	е		
Expected if "inert"	30.6	0.0	54.4	13.5	48.1	3.4	0.0	4.5
Measured	15.5		59.0	0	0	0		2.3



13 Dec '07			Af	ter gas	cleanin	g		
Expected if "inert"	18.8	4.9	51.0	8.7	20.3	8.7	0.0	0.0
Measured	10.8	0	47.6	0	0	0		
13 Dec '07	13 Dec '07 After CO ₂ capture							
Expected if "inert"	24.1	6.3	65.4	11.1	26.1	11.1	0.0	0.0
Measured	10.7	0	66.2	0	0	0		
19 Dec '07			Af	ter gas	cleanin	g		
Expected if "inert"	17.3	4.3	41.6	1.2	9.9	8.5	0.0	0.0
Measured	14.2	0	36.4	0	0	0		
19 Dec '07			Af	ter CO ₂	captur	e		
Expected if "inert"	22.7	5.6	54.5	1.5	13.0	11.2	0.0	0.0
Measured	10.6	0	55.2	0	0	0		

Inspection of the table above shows that a number of species are indeed "inert". Their variation is within the accuracy limits indicated.

Di-nitrogen oxide, N_2O , belongs to this category and so does carbon monoxide, CO. The essential message is that these gases do NOT end up in the CO_2 product, at least not within the detection limits!

Other species, in particular nitrogen dioxide, NO_2 , ammonia, NH_3 and hydrogen chloride, $HC\ell$, disappear completely from the gas in the cleaning section. In particular in the case of $HC\ell$, this is a strong argument for the Sargas concept.

Although it appears that all sulphur dioxide, SO₂, is also taken out of the gas in the cleaning section it is doubtful whether that is the case.

Detection difficulties in the wet gas (in particular the flue gas feed into the plant), however, seem to indicate too low levels of SO_2 especially during the December sessions.

For that reason, the data obtained from the Fortum control room data-logging system, graciously provided by Mr. Jonas Sampfors, were used to obtain a more realistic sulphur load for the plant as used in the earlier discussion of absorbent purity (section 2).

To estimate the sulphur load in the "combustor flue gas" from "entrance of stack", RSE assumed that a reliable measurement available from both the OLLEMO and Fortum data would be the CO₂ concentration in the gas.



The factor, Fc, relating impurities concentrations between stack and combustor is expressed as:

The rescaling for the measurements (dry or wet basis) is trivial.

Based on this equation, the estimates reported in section 2, indicate that some 50.8 %m of all sulphur components (SOx) was absorbed in and reacted with the absorbent. In the next section, the liquid phase analyses of the cleaning section will be further scrutinized to pinpoint the faith of $\sim 50 \text{ }\%\text{m}$ of the sulphur components; it can be safely assumed that they do not appear in the exit gas of the capture system.

Nitrogen oxide, NO, disappears only partly from the flue gas.

Inspection of the data table reveals that the gas cleaning section takes out a rather variable amount of $26.8 \, \text{km} \, (15 - 32 - 43 - 18 \, \text{km})$.

The rather high average temperature (NO reactions have an atypical inverse temperature response), the short residence time and the low oxygen contents of the flue gas is a plausible reason for this effect.

Another adverse effect is that NO in itself is rather inert (for the reaction chains see the overall assessment of the cleaning in section 2); NO needs multiple steps before it can be absorbed in the liquid phase. Even then, the volatile and weak nitrous acid, HNO₂, may reevaporate from the acidic scrubber or condenser liquid.

Addition of alkaline such as potassium carbonate, to the scrubber seems a secure way to increase cleaning efficiency. This for the same reasons as discussed earlier for SO₂ which is also absorbed as a weak acid in water.

The total removal percentage from the gas over the complete CO_2 capture plant of nitrogen oxides is a quite impressive 52.4 %m (51 – 49 – 56 – 53 %m).

Making the balance for the reactive nitrogen components (section 2) reveals: Of the total exposure to NOx:



47.6 %m leaves the capture system as NO

26.8 %m is captured in the gas cleaning section

17.5 %m reacts with the absorbent - without countermeasures in the cleaning section (e.g. K_2CO_3)

Some 8.1 %m is "missing" and might have been ab- and desorbed with the captured CO₂

The concentration of hydrogen fluoride, HF, is too small to be measured reliably; it appears to vanish, as expected, in the same way as hydrogen chloride does.

5. Vanadium content of the gas

The goal set for the 28-Feb campaign was to collect direct evidence for the low vanadium concentration in the cleaned gas from the CO₂ capture plant.

In this way, the indirect evidence presented for this (see below) could be strengthened.

Apart from a "blank" sample, which was not analyzed, a series of 1 ℓ gas samples was taken at OTP with so-called gas-bombs (cylinders) as follows:

Gas-bomb sampl s								
Timestamp	Туре	#						
Feb '08 14:50	Blank	1						
Feb '08 15:00	Clean gas	3						
Feb '08 15:07	Clean gas	4						
Feb '08 15:10	Clean gas	5						
Feb '08 15:15	Clean gas	6						
Feb '08 15:50	Flue gas	2						



The analysis was to proceed as follows:

Cool down the samples from operational conditions and keep them in the upright position

As temperature, water partial pressure and pressure go down the water contained in the gas condenses.

The condensate is allowed to collect slowly at the bottom of the upright cylinders over a period of some 14 days

The condensate is extracted from the bottom of the gas-bombs All liquid samples are weighed and analyzed for vanadium

As neither the weight nor the amount of condensate extracted by Analytica is mentioned in their report, an algorithm was devised to calculate the amount of condensate in the gas-bombs.

On average, the amounts are very small:

Clean gas: 160 µℓ

Flue gas: 582 µℓ

These numbers fit with the extracted amounts communicated verbally by Analytica on March 31 2008. Analytica used a 200 $\mu\ell$ syringe to transfer the condensate in a cuvette.

a. Analysis of the clean gas

The analysis of the sampling results was performed for both the average conditions of the whole measurement session, some 8 hours, as well as for the individual 1minute-average condition at the moment the samples were taken.

Clean gas samples using average OTP & measured water contents									
			Partial		Density				
	Temperature	Pressure	pressure	H_2O	H ₂ O	Condensate			
State H2O	vapor								



	С	K	bar	bar	%v	g/ℓ	µℓ H₂O
Warm 69.4 34	2.55 10.27	0.288 2.80	6.533 Co	d 25.0 298.15	7.42 0.032	5.360 160	

The results are collected in the flowing tables.

Clean gas samples using OTP & calculated water contents									
Sample 3	Tempe	rature		Partial Pressure pre H₂C	Density H ₂ O vapor	Condensate			
State	С	K	bar	bar	%v	g/ℓ	µℓ H₂O		
Warm	71.2	344.32	9.97	0.328	3.29	6.310			
Cold	25.0	298.15	6.84	0.032		5.001	184		

Clean gas samples using OTP & calculated water contents										
Sample 4	Tempe	rature		Partial Pressure pre H ₂ C	Density H ₂ O vapor	Condensate				
State	С	K	bar	bar	%v	g/ℓ	μ€ Η₂Ο			
Warm	71.2	344.35	10.09	0.328	3.25	6.385				
Cold	25.0	298.15	6.92	0.032		5.061	185			

Clean gas samples using OTP & calculated water contents							
		Partial	Density				
Sample 5	Temperature	Pressure	H ₂ O	Condensate			



		pressure vapor H₂O H2O							
State	C	K	bar	bar	%v	g/ℓ	µℓ H₂O		
Warm	71.3	344.41	10.05	0.329	3.27	6.359			
Cold	25.0	298.15	6.89	0.032		5.036	185		

Clean gas samples using OTP & calculated water contents									
Sample 6	Tempe	rature		Partial Pressure pre H₂C	Density H₂O vapor	Condensate			
State	С	K	bar	bar	%v	g/ℓ	µℓ H₂O		
Warm	71.2	344.32	10.21	0.328	3.21	6.462			
Cold	25.0	298.15	7.01	0.032		5.125	184		

Combining the above amounts of condensate with the reported analyses allows calculation of the amounts and concentrations in the clean gas:

Vanadium	Sample	# 3	# 4	# 5	# 6	Average
V concentration in condensate	μg/ℓ	6.62	1.48	1.12	0.838	2.51
Condensate	mℓ H₂O	0.160	0.185	0.185	0.184	0.179
V amount in 1 & gas sample at OTP	μg	0.00106	0.00027	0.00021	0.00015	0.00045



V concentration in	μg/m³	1.06	0.27	0.21	0.15	0.45
clean gas	P-0/ · · ·		0.27	0	0.20	

Remarkably, the sequence of at which the samples have been taken seems to be important, as can be seen in Figure 1.

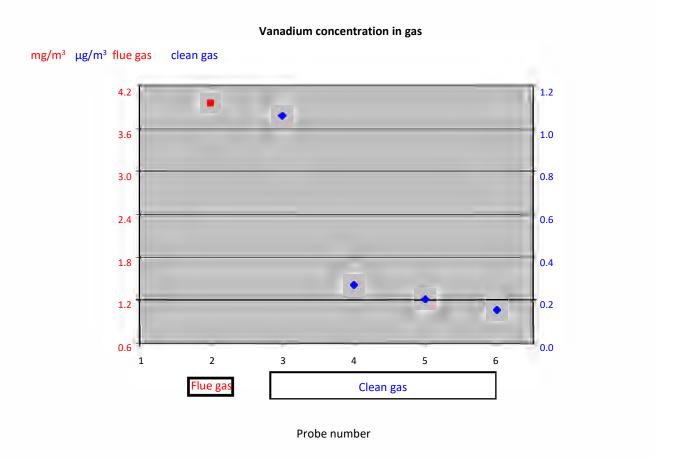


Figure 1. Vanadium concentrations in the Sargas Värtan DEMO plant gasses.

One explanation of the downward trend in the vanadium values for the consecutive samples may be that the sampling line or the station itself still contains some condensate in which vanadium leached from the stainless steel tubing is present. These effects – in absolute numbers – are small.

All concentrations are very low and at the limit of detection of the methods used.

The gas is therefore essentially vanadium free.



b. Analysis of the flue gas

The analysis of the flue gas samples posed some problems because of the presence of dust and unexpectedly high concentrations of vanadium observed in the condensate.

Therefore, two different methods were used by ALS Analytica to verify the correctness of the result and eliminate falsification of the results due to interference from other metals, such as tungsten.

The different chemical analysis methods proved to give consistent results.

Although only one sample of the flue gas was taken, the evaluation was also made using both the average plant sampling conditions of the whole measurement session of ~8 hours and the individual 1-minute-average condition at the moment the sample was taken.

However, the on-line data from the Värtan control room are no longer available at this point and, as indicated earlier, no detailed gas concentration data are available as yet from OLLEMO.

Therefore, both evaluations rely on the average measured water content of the flue gas to determine the water condensate. Since the gas is not saturated, measurements are required to determine water contents – in contrast to the clean gas. The results are collected in the flowing tables.

Flue gas samples using average OTP & measured water contents							
State	Tempe	erature	Pressure	Parti	al	Density H₂O vapor	Condensate
pressure H2O 2O H	С	K	bar			g/ℓ	µℓ H₂O
				bar	%v		
Hot	237.7	510.85	10.67	1.419	13.30	4.551	
Cold	25.0	298.15	2.29	0.032		1.677	582

Flue gas samples using OTP & calculated water contents						
			Partial		Density	
Sample 2	Temperature	Pressure		H_2O	H₂O vapor	Condensate
			pressure H2O		g/ℓ	



						•	
State	С	K	bar	bar	%v		μℓ H₂O
Hot	232.6	505.76	10.73	1.427	13.30	4.623	
Cold	25.0	298.15	2.28	0.032		1.665	591

Combining the above amount of condensate with the reported analysis allows calculation of the amounts and concentrations in the flue gas:

Vanadium	Sample	# 2	
V concentration in condensate	μg/ℓ	6680	
Condensate	mℓ H₂O	0.591	
V amount in 1 ℓ gas at OTP	μg	3.95	
V concentration in clean gas	mg/m³	3.95	

The single result (note the units!) is included in Figure 1.

Since no likely volatile components are available, the vanadium in the flue gas could have two sources:

Coal and hence a constituent of the dust carried by the flue gas Leaching of vanadium by acidic gasses (especially HCl) from the (stainless) steel and settled dust, ending up in the condensate.

With an average dust load of \sim 93 mg/m³, the above analysis suggests that the vanadium content in the dust is some 4.25 %w. The concentration of a likely chemical species such as V_2O_5 must be even higher, which is unlikely.

c. Follow-up on the vanadium source



Fortum offered help in tracking a suspected vanadium source in the flue gas as discussed above. Samples were collected and analyzed from

The coal

The PFBC bed ash

The dust from the cyclone

The results are as follows:

Flue gas Vanadium	Vanadium content		
Source	mg/kg		
Coal	70 ~ 140		
PFBC bed ash	50 ~ 60		
Cyclone dust	90 ~ 140		

When one assumes that the composition of the residual dust after cyclones, which is the dust carried by the flue gas to the turbine and to the DEMO plant, matches that of the cyclone dust, its average vanadium level is ~115 mg/kg dust.

The flue gas entering the DEMO plant has an average dust load of \sim 93 mg/m³, which means that the dust contains 10.7 μ g/m³.

As was shown earlier, the flue gas produces \sim 580 $\mu\ell\ell$ condensate. When all the dust is captured in the flue gas condensate, one would expect to find a vanadium concentration in the condensate of:

10.7 μ g/m³ / 0.580 ℓ/m³ = 18.5 μ g/ℓ condensate.

Three conclusions follow from this result:

This amount of vanadium is more realistic but far less than the sample analysis

The high concentrations analyzed could be due to leaching from dust as well as from
stainless steel



The flue gas vanadium concentration in the Värtan plant has always been 2 orders of magnitude **higher** than in the clean gas from the CO₂ capture system. This is irrespective of whether the Analytica result stands or not.

These conclusions lay to rest the reservations expressed by Siemens regarding vanadium: the gas turbines have always had to cope with more vanadium than the CO₂ capture plant releases!

6. Liquid impurity balance

Al liquid samples of the gas conditioning part of the DEMO plant were analyzed in two steps, each producing two sets of results. The liquid was first filtered and the filtrate analyzed. The filtered solids were then leached with acid and partly re-dissolved. This liquid is then analyzed as well.

The concentrations in the re-dissolved liquids are meant to be qualitative, and all have very low concentration in the $\mu g/\ell$ range. They effectively do not play any role in the balancing of the different impurities.

In order to interpret the ALS Analytica data for the liquid phase of the scrubber, the condenser and the humidifier an estimate of the liquid flow through these apparatus is required. No flow meters are installed for the discontinuously controlled levels in the bottom of the apparatus, mainly to secure the pumps of the recycles.

In the scrubber a certain amount of water is constantly evaporated to coal the flue gas an catch residual dust.

This water is continuously pumped around and saturates slowly with gaseous impurities from the flue gas.

Water is periodically drained and replenished from the bottom. This process, which is done automatically by the process computer, ensures that an equilibrium situation is created and maintained.

The operators survey these actions and ensure the computer settings are such that the "renewal rate", the rate at which the water is renewed, is approximately three times the amount of water evaporated. In this way, the equilibrium is not disturbed and excessive accumulation is avoided.



This information can be used to estimate the removal of impurities from the gas by the scrubber.

For the duration of the gas measurement sessions, the relevant data are:

Scrubber	Units	15 Nov '07	13 Dec '07	
Total flue gas flow	kg/h	40.4	36.8	
Δ Temperature	°C	119	84	
Evaporation rate	kg/h water	2.47	1.59	
Renewal rate	ℓ/h	7.80	5.04	

The analysis results for the filtrate of the scrubber, collected below, show some surprises:

 The filtrate appears to contain a surprisingly high amount of potassium and sodium.

In particular the potassium seems to be derived from the coal combustion.

- The sodium may be brought into the system by the water the scrubber requires; the scrubber is not using de-mineralized water.
- Quite some nitrogen compounds are washed out of the gas by the scrubber, inspection of the results shows that most of it is ammonia.
- The scrubber is very effective in removing chlorine and, as expected, less so in the removal of sulphur.

The dropped efficiency of the scrubber, as exemplified by the December 13th results, confirms the operators' suspicions that running the apparatus with acidic recycle may have caused corrosion of the restriction of the recirculation line. This restriction ensures a pressure build-up for the water injection and had caused some problems.

As a result of the acidic recycle, the ammonia removal is, as expected, almost complete in the scrubber.



Scrubber	К	Na	S	N _{tot}	NH ₃ -N	Cℓ
Filtrate			mį	g/ િ		
15 Nov '07	5.1	14.1	11	50	49	193
13 Dec '07	3.6	12.4	18.2	39	37	112
Removal rate			mg/h			g/h
15 Nov '07	39.8	110.0	85.8	390.0	382.2	1.51
13 Dec '07	18.1	62.4	91.7	196.6	186.5	0.56
Gas feed rate			mg/h			g/h
15 Nov '07			218	860		1.72
13 Dec '07			835	1381	218	1.10
Scrubber efficiency			%	w		
15 Nov '07			39	45		88
13 Dec '07			11	14	86	51

The captured dust, which was expected to contain enough reactive calcium and magnesium to neutralize the solution, is apparently not capable to keep the recycle alkaline.

This observation is not a drawback for the Sargas concept; it merely confirms the expectation. A remedy is readily available for implementation.

The condenser ensures the essential conditioning of the flue gas before it is fed into the CO_2 absorption column.

The apparatus essentially controls the absorption temperature of the flue gas and ensures saturation. The latter is of great importance to maintain the efficiency of the absorption process itself.

The condenser is a recirculation column and provides an extra countercurrent wash-effect of the flue gas.



Since the flue gas leaving the scrubber is, as a rule, hotter than the target temperature for absorption, the condenser will be normally true to its name and produce condensate.

As a beneficial side effect, it can also absorb remaining gaseous impurities (and even dust) from the flue gas. To assess and quantify this effect, one needs to proceed in an analog fashion as for the scrubber.

As water is discontinuously and automatically removed by the process computer and no flow meter is available, the rate of condensate removal has to be estimated. Here too, the operators ensure that the bulk of the liquid is reaching equilibrium with the gas, by keeping the average level in the bottom of the apparatus constant.

In order to interpret the efficiency and track impurities one has to estimate from the indirect measurements how much condensate is produced. For the duration of the gas measurement sessions, the relevant data are:

Condenser	Units	15 Nov '07	13 Dec '07
Total "dry" flue gas flow	m³/h	5.70	5.15
Pressure	bar	10.3	9.9
Gas temperature condenser feed	°C	110.1	115.0
Gas temperature condenser exit	°C	101.6	77.1
P _{H2Oin}	bar	1.44	1.69
P _{H2Oout}	bar	1.07	0.42
Condensation rate	kg/h water	1.28	4.27
Removal rate	ℓ/h	1.34	4.38

The reported concentration data can now be interpreted as follows:

Condenser	К	Na	S	N_{tot}	NH ₃ -N	Cℓ
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Filtrate			mį	g/ℓ		
15 Nov '07	1.4	4.7	1.3	49		203
13 Dec '07	10.7	6.2	16.4	55	37	60
Removal rate			mg	g/h		
15 Nov '07	1.9	6.3	1.7	65.7		272.0
13 Dec '07	46.9	27.2	71.8	240.9	162.1	262.8
Gas feed rate			mg/h			g/h
15 Nov '07			218	860		1.72
13 Dec '07			835	1381	218	1.10
Scrubber efficiency			%	w		
15 Nov '07			0.8	7.6		15.8
13 Dec '07			8.6	17.4	74	23.9

- The filtrate appears to contain a much lower amount of potassium and sodium than the scrubber, as is to be expected. Although here too normal process water from the Fortum plant is used in filling the vessel for startup, this is a much smaller amount than the permanent feed to the scrubber.
- Remarkably, the (Na / K) ratio is very similar to the one seen in the scrubber this fact also points to contamination from water, rather than from the coal.
- As is evident from the amounts of acidic components absorbed from the gas, up to 17 %w of the total nitrogen and up to 24 %w of the chlorine, the recycle is slightly acidic under these conditions.
- The total nitrogen removal of some 50 %w, matches within bounds, with the combined scrubber-condenser results.
- Sulphur removal is rather marginal in the condenser. When combined with the scrubber data, the $^{\sim}$ 50 %w removal of sulphur before absorption is consistent with the findings that no sulphur is present in the cleaned gas and that 50 %w is found to have reacted with the absorbent.
- The chlorine removal percentages match with those of the scrubber confirming that no chlorine is found in the absorbent.



• At face value, the reliability of the either ammonia-nitrogen determination in the liquid or the gas measurement has to be questioned. At least during the December sampling period, more NH₃ is removed than is brought in by the flue gas.

The liquid phase analysis of the humidifier, which does the final conditioning of the cleaned flue gas before it leaves the capture plant, does not aim at finding flue gas born impurities. The same hold for the analysis of condensate from the clean gas pipe.

The cleaned gas from the Sargas Värtan DEMO plant is not fed into the Fortum gas turbine. However, one goal of the DEMO plant is to show that is gas of high purity and that no compounds that could originate from the CO₂ capture plant are carried to the turbine.

In particular, components such as vanadium and potassium could harm the turbine and cause extra maintenance and possibly shorten its lifespan.

It is clear from the presented data, that the CO_2 capture system cleans the gas from gaseous impurities, such as HC ℓ , thus improving the quality of the gas with respect to the actual operation.

With the results of the chemical analysis of the humidifier and gas condensate, presented below, an assessment of the concentration of compounds "intrinsic" to the capture system becomes possible.

	Humidifier			Clean gas condensate		
Filtrate Traces	K	В	V	К	В	V
	µg/ℓ					
15 Nov '07	64.4	1910	1.5	3.3	299	1.4
13 Dec '07	18.1	1220	0.5	76.1	3080	1890

As is apparent, all numbers are expressed in $\mu g/\ell$; all concentrations are very low.



• Remarkably, in the humidifier liquid one finds a K / B / V ratio that remotely resembles the liquid composition.

The indicative ratio for the liquid is, in mass units, K/B/V = 31/1/1.

For both measurement periods, the K / V ratio complies with the liquid. The obvious conclusion is that the absorber is causing a minute amount of spray, allowing droplets to be dragged with the gas and which then end up in the humidifier acting as a countercurrent scrubber.

- The very simple and non sophisticated construction at the top of the absorber (mainly because of restrictions on the column height and time pressure) may be one cause for this.
- A second plausible cause is the rather high absorbent recycling rate used by the operators to gain more safety margin. Spraying of the liquid when

entering the column may well be a consequence of the high entrance speeds this mode of operation causes.

- In any case, the amount of spray apparently remains very low iand is no cause for alarm.
- The same phenomenon is not observed in the condensate, where all K / B / V
 ratios are off by orders of magnitude from the liquid. A safe conclusion is that the
 humidifier is very effective and with potassium and vanadium vanishingly there is
 no need to fear for the turbine.
- The data point to yet another phenomenon in that the boron concentration is rather high and over-proportional with respect to both other analyzed components.

This situation is, in fact, apparent in both samples and during both sessions.

• Boron, is the only components, that under certain circumstances may become volatile. The volatile form is boric acid, H₃BO₃.

Although it not obvious how boric acid could exit in the very alkaline absorbent solution, a certain minute equilibrium amount is present even in the pH 10~12 environment of the absorbent.

Volatilization could happen when the temperature is too high ($^{\sim}155$ °C), when the absorbent concentration is very high ($^{\sim}40$ %w) or when the degree of saturation of the carbonate with CO₂ is high ($^{\sim}65$ %m).

• In the course of the DEMO runs, all of the above situations did occur, separate and in combination.



- Additional heating to compensate over-proportional heat loss and lower than design flue gas temperatures using high temperature steam could cause local overheating of the absorbent entering the absorber
- Neglect or inaccuracies in the hand-bookkeeping of the water household could and did lead to high average concentrations with water deficits being as high as 80 kg. Concentrations at that point could be over 35%w locally.
- Fluctuations in the water feedback to the absorbent, especially during the December session when a special configuration, "water bypass", has been put in operation could have caused a systematic higher absorbent concentration.
- High degrees of saturation in the absorbent, in which the acidity of the extra CO₂ causes an increasing pH drop is the most likely cause for boric acid volatility. The simple method created for judging the saturation available by the operators depends heavily on accurate water bookkeeping. At some points in time, average saturation has been as high as 75 %m. This situation was sometimes created on purpose the test the boundaries of operability of the concept.
- For all the above reasons, the high boron concentrations are not intrinsic to the concept.
- Moreover, a simple remedy to avoid boron is available in that an alkaline "shield" is used in the humidifier.
- The extremely high vanadium concentration in the condensate reported for the
 December measurement session is hard to explain and will be verified separately.
 If its origin is within the capture process, it indicates that either a volatile
 vanadium component within the gas phase or a contamination from maintenance
 is involved.
- The completely non-proportional ratio between vanadium and potassium excludes that the concentration is produced from the absorbent. The extreme difference between the low concentrations in the humidifier liquid and the "gas phase deposits" exclude droplet spray from the humidifier as a source.
- The only family of relatively volatile components comprises the very unstable vanadium chlorides. Their formation in the strongly alkaline solution is thermodynamically very improbable and since no chlorides are found in the absorbent, these components must be ruled out as candidates.
- Since only one analysis result shows this abnormally high value this will require
 more investigation. Analysis of discrete gas samples are planned to search for
 vanadium, directly in the gas.



Because of the complicated nature of dust measurements, they were excluded from the goals for the DEMO plant. However, as in indicator for the capture of the dust and the degree in which the alkaline nature of it (by virtue of some excess dolomite) might be helpful, some indirect analyses have been done.

In the hope that the liquid samples from scrubber and gas condensate are well-mixed and keep eventual solid dust particles suspended, these samples were filtered. The filter residue was then leached in acid and analyzed again.

Calcium, in as far as it has not been transformed into sulphate, will dissolve and is useful as a qualitative indicator for dust capture (together with the total weight of the filter residue.

Clean gas condensate is produced "ad hoc" and not continuously by cooling a pipe segment and temporarily forcing condensation. The concentrations are an indication of pipe deposits only. The raw results are collected in the following table.

	Scrubber			Clean gas c	ondensate		
Residue Traces	Ca	Mg	Hg	Fe	Residue	Са	Residue
		μg			g	μg	mg
15 Nov '07	21.2	<8	0.7	0.8	4	34.7	12
13 Dec '07	53.3	34.1	1.1	67.2	106	23.1	16

It appears that the scrubber fluid contains a large amount iron (Fe).

- The dust from combustor does not contain iron in significant amounts.
- The high iron contents of the solids, therefore, must be the results of corrosion in the scrubber.
- The corrosion products are obviously insoluble in the slightly acidic scrubber water; it follows that the most likely iron species making up the bulk of the iron in the suspended particles is Fe₂O₃.
- Using this assumption, more realistic estimates of the dust in the scrubber samples can be made:



	Scrubber					
Residue correction	Fe	Fe ₂ O ₃	Dust	Sample volume	Renewal rates	Dust removal rates
			estimate			
		mg		тℓ	ℓ/h	mg/h
15 Nov '07	0.8	1.1	2.9	456	7.80	49.6
13 Dec '07	67.2	96.0	10.0	405	5.04	124.4

It appears that the scrubber does not have to cope with a large amount of dust. This confirms the observation that the samples and the bulk of the liquid in the scrubber are clear and does not – in contrast to expectations – have the constitution of light slurry.

The huge pump-around of the scrubber helps to support the assumption that the samples are representative for captured dust.

The low dust contents of the scrubber samples is an indication of the excellent performance of the gas filters which leave only the very finest dust (< 2 μ m) in the scrubber.

Information of Fortum's long term averaged data for dust levels in the flue gas was used to estimate the dust contents after combustor at ~93 mg/m3 and obviously prone to variation.

This data was used to put the scrubber dust removal efficiency in perspective:

Duet	Scrubber				
Dust removal efficiency	Flue gas feed rate	Dust input capture	Scrubber removal		
	m³/h	mg/h	%w		
15 Nov '07	6.6	613	8		
13 Dec '07	7.2	666	18.7		

In view of the size distribution of the dust after the secondary cyclones of the combustor, with fine dust of particle size $> 2 \mu m$ being present at



 \sim 10 % percentile, the estimates of the residual dust load in the scrubber seems realistic.

Some confirmation of the higher dust contents of the combustor gas during the December campaign and not only during the measurement session, was found in the operators logbook. The flushing frequency of the gas filters (which is triggered by pressure drop build-up) had to be increased during this period.

No relevant conclusions can be derived from the huge variation in magnesium contents of the samples at this point. It does not appear to be the consequence of a single type of equilibrium system, such as CaCO3 – SO2 in the combustor.

Magnesium levels in the water have not been checked.

Mercury levels seem to indicate that at least the non-metallic mercury adheres to the dust.

8. Quality of produced CO₂

During the latest two campaigns of the DEMO plant in February and March, the CO₂ quality has been tested by on-line gas chromatography by OLLEMO.

The following tables are copied from the report and show that during both measurement sessions **NO** gaseous impurities from the flue gas were detected in the CO₂.

The detection limit is 1 ppmv for most components except SO2, where it is 2.5 ppmv when the gas is wet and NH3 were the limit is 0.5 ppmv.

These results show that, in contrast with what has been suggested as a possibility in the technical report on the chemical analysis (February 19), NO is **NOT** desorbed into the CO₂ product.

The results also confirm that the CO_2 is free from N_2O .

Gas chromatography measurement results of the produced CO₂.

28 Feb '08 Incoming CO2 produc	t:
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H₂O %v	13,3	
CO ₂ %v	16,6	100
NO ppmv dry	13,6	<1
NO ₂ ppmv dry	<1	<1
N₂O ppmv dry	31,1	<1
NH₃ ppmv dry	15,7	< 0,5
HCl ppmv dry	35,9	<1
SO ₂ ppmv dry	< 2,5	< 1
HF ppmv dry	<1	<1
CO ppmv dry	<1	<1

05 Mar '08	Incoming flue-gas	CO ₂ product
H₂O %v	13,1	
CO ₂ %v	16,5	100
NO ppmv dry	12,4	<1
NO ₂ ppmv dry	<1	<1
N₂O ppmv dry	28,8	<1
NH₃ ppmv dry	<0,5	< 0,5
HCl ppmv dry	26,5	<1
SO ₂ ppmv dry	< 2,5	<1
HF ppmv dry	<1	<1
CO ppmv dry	< 1	<1



Some impurities were, at the time of the measurements, not present in the flue gas in concentrations higher than the detection limit such as NO₂, SO₂, HF and CO but are by their nature not expected to be found in the CO₂.

The gas chromatograph was not equipped to sense N₂, O₂ and Ar but the gas was dried before entering the apparatus.

In a recent publication (AirProducts 2008) an acceptable limit for the total of these gasses in the produced CO_2 has been suggested to be < 4 %v, for oxygen the suggested limit was stated as 100 ppmv.

Using the Siemens data in their Sargas feasibility report (2007) the expected N_2 level is ~ 2 %v for a Sargas plant.

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Chief Engineer

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