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ABSTRACTS BOOKLET

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SUSTAINABLE DEVELOPMENT



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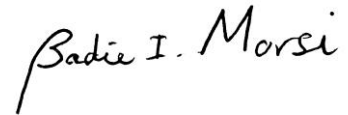
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On behalf of the Twenty-Eighth Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Ms. Heidi M. Aufdenkamp for her dedication and professionalism; and Mr. Yannick Heintz and Mr. Laurent Sehabiague for their invaluable assistance in preparing this Abstracts Booklet.

Thank you,

A handwritten signature in black ink that reads "Badie I. Morsi". The signature is written in a cursive style with a large initial "B" and "M".

Badie I. Morsi, Editor
Professor and Executive Director of the Conference

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SESSION 1

Major CCS Demonstration Projects: Financing of CCT and CCS Projects

Carbon Markets: Unlocking Value Through Political Risk Insurance

Antonio Barbalho, The World Bank Group, USA

Regulatory framework uncertainties and ineffective market rules has led the carbon markets potential to remain unfulfilled with embedded funding scarcity. Perhaps the carbon markets may be experiencing a change process just comparable to the industrial revolution in 1800's with far reaching implications to the world's economies. Despite such challenging environment, few projects are coming to fruition based on simple business rules: managing transition through bounded-stability. Political risk insurance could bring such stability to projects across different markets and technologies. The World Bank/MIGA has taken steps to pioneer its support to investments from exploration (feasibility) to operations in the carbon markets enabling private equity, lenders and developers to achieve sustainable results.

Financing Energy Sustainability – Efficiency and Conversion to Reduce GHG

Robert A. Payne, Cate Street Capital, Inc., USA

Imposition of more stringent emissions standards by both federal and state environmental agencies, coupled with higher operating costs, is driving many smaller coal-fired utilities in the United States to either suspend or dramatically curtail operations. In Europe, the imposition of carbon emissions standards has fundamentally changed the fueling strategies of many utilities, leading to the rapid development of biomass fuel demand. This discussion will focus on how these smaller coal-fired power plants may be revitalized by modifying their fuel mix to meet emissions standards and reduce operating costs. Projects can be successfully financed by capitalizing on federal and state programs supporting renewable energy generation. In low-income or high unemployment areas, availability of New Market Tax Credits can be used to complement more conventional financing.

SESSION 2

Gasification: General – 1

An Overview of U.S. DOE's Advanced Gasification Technologies Program

Jenny B. Tennant, DOE/NETL, USA

The U.S. Department of Energy's (DOE) Gasification program's vision is to use gasification to turn coal into power with carbon dioxide (CO₂) sequestered, while supporting the highest environmental standards. The Gasification Technologies Program has a history of success in technology development and demonstration. The current program research and development portfolio will enable deployment of the clean and affordable energy systems required for growing energy markets. The program is currently supporting several major projects, such as: (1) demonstrating novel, efficient, and cost-effective high-temperature gas cleaning technology integrated with carbon capture and storage; (2) developing a non-cryogenic air separation technology with lower capital cost and energy requirements than conventional cryogenic processes to produce high-temperature/high-purity oxygen from air by using ceramic ion transport membranes; and (3) developing a hydrogen transport membrane technology to cost-effectively separate hydrogen from shifted coal-derived syngas. Additionally, the program has been supporting the improvements in reliability, availability, and maintainability associated with gasification-based energy conversion systems. These and several other ongoing projects support DOE's vision of near-zero emissions power generation by reducing the cost and improving the efficiency of capturing CO₂ from syngas derived from coal.

This paper will present a comprehensive evaluation of the technologies being developed, along with a detailed review of advances in gasification-based technologies that will enable low-cost, low-carbon emission, coal-based energy systems.

Dispatchable Operation of IGCC

Donald J. Chmielewski, Benjamin Omell, Ming Wei Yang, Illinois Institute of Technology, USA

The Integrated Gasification Combined Cycle (IGCC) possesses a number of benefits over traditional power generation plants, ranging from increased energy conversion efficiency to flex-fuel and carbon capture opportunities. A less known benefit of the IGCC configuration is the ability to load track electricity market demands. The idea

being that material storage can be used to time-shift power production away from periods of low power value to periods of high power value. In this work, we present a supervisory control scheme, known as Market Responsive Control (MRC), which has the objective of maximizing revenue for a given level of plant dispatchability. The design of this controller is achieved by a fairly simple convex optimization problem. The MRC method is then embedded within an equipment design algorithm. This extended algorithm, known as MRC Embedded Equipment Design (MRC-EED), has the objective maximizing Net Present Value (NPV) in an effort to size the storage units as well as the required energy conversion devices. The design options considered in this study focus on hydrogen and compressed air storage as well as ramping abilities of the gasification block. Under the economic assumptions of this study, it is concluded that the NPV of the hydrogen storage option is significant, while that of compressed air is much less favorable. Finally, no scenario could be found in which ramping of the gasification block provided a positive NPV.

Advanced Virtual Energy Simulation, Training, and Research: IGCC with CO₂ Capture Power Plant

Stephen E. Zitney, Eric A. Liese, Priyadarshi Mahapatra, Richard Turton, Debangsu Bhattacharyya, DOE/NETL/AVESTAR Center; Graham T. Provost, Fossil Consulting Services, Inc., USA

In this presentation, we highlight the deployment of a real-time dynamic simulator of an integrated gasification combined cycle (IGCC) power plant with CO₂ capture at the Department of Energy's (DOE) National Energy Technology Laboratory's (NETL) Advanced Virtual Energy Simulation Training and Research (AVESTARTM) Center. The Center was established as part of the DOE's accelerating initiative to advance new clean coal technology for power generation. IGCC systems are an attractive technology option, generating low-cost electricity by converting coal and/or other fuels into a clean synthesis gas mixture in a process that is efficient and environmentally superior to conventional power plants.

The IGCC dynamic simulator builds on, and reaches beyond, conventional power plant simulators to merge, for the first time, a "gasification with CO₂ capture" process simulator with a "combined-cycle" power simulator. Fueled with coal, petroleum coke, and/or biomass, the gasification island of the simulated IGCC plant consists of two oxygen-blown, downward-fired, entrained-flow, slagging gasifiers with radiant syngas coolers and two-stage sour shift reactors, followed by a dual-stage acid gas removal process for CO₂ capture. The combined cycle island consists of two F-class gas turbines, steam turbine, and a heat recovery steam generator with three-pressure levels. The dynamic simulator can be used for normal base-load operation, as well as plant start-up and shut down. The real-time dynamic simulator also responds satisfactorily to process disturbances, feedstock blending and switchovers, fluctuations in ambient conditions, and power demand load shedding. In addition, the full-scope simulator handles a wide range of abnormal situations, including equipment malfunctions and failures, together with changes initiated through actions from plant field operators.

By providing a comprehensive IGCC operator training system, the AVESTAR Center is poised to develop a workforce well-prepared to operate and control commercial-scale gasification-based power plants capable of 90 percent pre-combustion CO₂ capture and compression, as well as low sulfur, mercury, and NO_x emissions. With additional support from the NETL-Regional University Alliance (NETL-RUA), the Center will educate and train engineering students and researchers by providing hands-on "learning by operating" experience.

The AVESTAR Center also offers unique collaborative R&D opportunities in high-fidelity dynamic modeling, advanced process control, real-time optimization, and virtual plant simulation. Objectives and goals are aimed at safe and effective management of power generation systems for optimal efficiency, while protecting the environment.

To add another dimension of realism to the AVESTAR experience, NETL will introduce an immersive training system with innovative three-dimensional virtual reality technology. Wearing a stereoscopic headset or eyewear, trainees will enter an interactive virtual environment that will allow them to move freely throughout the simulated 3-D facility to study and learn various aspects of IGCC plant operation, control, and safety. Such combined operator and immersive training systems go beyond traditional simulation and include more realistic scenarios, improved communication, and collaboration among co-workers.

NETL plans to continue building the AVESTAR portfolio of dynamic simulators, immersive training systems, and advanced research capabilities to satisfy industry's growing need for training and experience with the operation and control of high-efficiency, near-zero emission energy plants. The state-of-the-art simulation facilities are located at NETL in Morgantown, WV and at West Virginia University's National Research Center for Coal and Energy.

Enabling Clean Coal Power Generation: ITM Oxygen Technology

Lori L. Anderson, Phillip A. Armstrong, John M. Repasky, VanEric E. Stein,
Air Products and Chemicals, Inc., USA

In the late 1980's Air Products identified a class of perovskite ceramic materials with high flux and separation selectivity for oxygen ions. These materials have become the basis for a novel class of air separation technologies, referred to as Ion Transport Membranes (ITMs). Along with partners and through partnership with the U.S. Department of Energy, Air Products has made substantial progress in developing ITM Oxygen technology into a cost effective method of oxygen production. ITM Oxygen integrates well with advanced power generation processes, as well as traditional energy intensive industrial processes requiring oxygen.

The team has successfully demonstrated expected performance of commercial-scale modules in a prototype facility that produces up to 5 tons-per-day (TPD) of oxygen. Continued operation of this unit has verified thermal and pressure cycle performance, and tested a number of component designs and operating scenarios for next phase scale-up. Design of the next phase pilot unit is complete and operation is planned in 2012. This Intermediate Scale Test Unit (ISTU) is designed to produce up to 100 TPD of oxygen integrated with turbo-machinery and co-production of power. Data from the 100 TPD unit will provide the design basis for a much larger plant that could produce 2000 TPD. In parallel, work has also begun to expand ceramic fabrication capacity to support these demonstrations.

This paper will present an overview and update of the ITM Oxygen development effort, including testing of commercial-scale ceramic modules and operating scenarios, next-phase scale-up designs, ceramic manufacturing expansion work, and developing industrial power process integrations and economic analyses toward gasification, oxy-combustion, and other energy-intensive industrial applications. A commercialization timeline will be discussed.

SESSION 3

Coal-Derived Products: General – 1

Development of a Fluidizable Catalyst and Transport Reactor-Based Methanation Process for the Conversion of Syngas into Pipeline Quality Natural Gas

Jason Trembly, Brian S. Turk, Jon McCarty, Maruthi Pavani, Jian-Ping Shen,
Raghubir P. Gupta, RTI International, USA

The convenience, clean-burning attributes, and lower carbon intensity of natural gas compared to coal and other hydrocarbon fuels make it the primary choice for industrial, commercial, and residential power and heating requirements. In certain regions of the world, dwindling supply adversely affects natural gas cost and availability while increasing dependency upon foreign imports. One approach for supplementing domestic resources of natural gas is conversion of coal into a methane-rich product or substitute natural gas (SNG), which meets current natural gas pipeline specifications. The main advantage of this approach is that this SNG product can be introduced into the extensive natural gas pipeline network increasing supply without any noticeable effect to the end user while enabling CO₂ capture and sequestration from the coal conversion process. The technical challenge is to develop processes for converting coal into SNG that are thermally efficient, environmentally attractive, and economically competitive.

Conventional technologies for the production of SNG from coal-derived syngas consist of a series of fixed-bed reactors with interstage cooling, product recycle, or a combination of both to extract heat generated by the methanation reaction. Although these processes have been commercially proven, each has significant capital and operating costs associated with multiple fixed-bed reactors and recycle compressors. RTI, with DOE/NETL support, is developing an innovative transport methanation process utilizing transport reactor and solids cooler technologies used commercially in fluid catalytic crackers for petroleum refining to convert syngas into SNG with significantly lower capital and operating complexity compared to conventional methanation processes. The transport methanation process utilizes circulating solid catalyst to adsorb reaction heat, effectively moderating temperature rise across the reactor significantly increasing conversion, while heat is removed from the catalyst in a solids cooler producing high-quality saturated steam.

RTI developmental progress for the transport methanation process includes preparation, and production scale-up of attrition resistant fluidizable methanation catalysts, pilot-scale testing of a scaled up catalyst sample, process simulation, and computational fluid dynamics of the transport reactor. This presentation will describe results from this development program.

SESSION 4

Carbon Management: CO₂ Capture - Sorbents – 1

A Rigorous Yet Scalable Kinetic Model for the Uptake of CO₂ By Silica-Supported, PEI-Impregnated Sorbents

David S. Mebane, Daniel Fauth, McMahan Gray, DOE/NETL, USA

A particle-level model for the dry adsorption of CO₂ in mesoporous silica-supported poly(ethyleneimine) (PEI) sorbents has been proposed. The model incorporates chemical, transport and microstructural components. Key assumptions of the model are chemical ideality, isothermal conditions, microstructural stability and hierarchical porosity. The known zwitterion mechanism for CO₂ adsorption in aqueous amines is utilized for both the adsorption itself and for diffusion of CO₂ in PEI. A microstructural model is derived which divides the space into three length scales. At the highest length scale, (the level of macroporosity), gas diffusion is considered to be infinitely fast. Knudsen diffusion takes place at the intermediate length scale, while solid-state diffusion takes place at the smallest length scale. The final reaction-diffusion model consists of a set of coupled partial differential equations that can be solved through an iterative, line-by-line method. The model results in twelve free model parameters to be fitted to experimental data. Qualitatively, the model is seen to reproduce the principal features of thermogravimetric measurements on two silica-supported, PEI-impregnated sorbents synthesized at the National Energy Technology Laboratory.

PEI-Silica “Nanobubbles” for CO₂ Sorption

Karen Uffalussy, Götz Vesper, University of Pittsburgh/DOE/NETL; Craig
Stevenson, Lu Whaley, University of Pittsburgh, USA

Recent efforts have focused on combining the advantages of solid capture materials with those of liquid amines by both grafting and embedding amine groups onto solids. Here, we report on the application of this sorbent design principle to the encapsulation of polyethylenimine (PEI), a liquid amine widely used for CO₂ capture, in silica “nanobubbles”. By utilizing a nanostructured silica with well-defined and finely controllable dimensions we aim not only to synthesize an inexpensive and efficient hybrid amine-silica sorbent, but also to identify the key structural parameters which affect the capture capacity of encapsulated amines.

Porous silica shells were prepared in a reverse microemulsion using a straightforward one-pot synthesis method developed in our laboratory. The resulting “nanobubbles” consist of a microporous silica shell with wall thickness (which can be tailored between ~4-30nm) encapsulating a pronounced cavity of ~15 nm diameter. PEI was introduced into these porous silica nanobubbles by a simple wet impregnation approach, resulting in PEI loadings of ~25 – 75wt%. The CO₂ sorption kinetics were then measured via isothermal thermogravimetric analysis (TGA) over a temperature range of 60 – 105°C during alternating exposure to a high purity CO₂ stream (P_{CO₂} = 1 bar), followed by desorption in pure He stream at the same temperature.

Results show distinct contributions from kinetic and thermodynamic effects with increasing temperature, and, more importantly, a drastic acceleration of the sorption kinetics for the nanoencapsulated PEI in comparison to the free liquid PEI by about three orders of magnitude. Furthermore, the specific CO₂ sorption capacity (per mole of PEI) is twice as high for the nanoencapsulated PEI than for the unconfined liquid PEI (~125 mg CO₂/g PEI vs ~250 mg CO₂/g PEI, respectively). The strongly accelerated kinetics can be explained by the drastic reduction of the diffusion length for the nanoconfined material, and hence a complete removal of mass transfer limitations during CO₂ capture. The reason for the enhanced sorption capacity is still under investigation, but is likely due to configurational changes of PEI in the nanoconfinement.

Overall, the nanoencapsulated PEI shows great promise as a hybrid liquid-solid CO₂ sorbent material, and results to-date suggest that further improvement of the performance will be possible based on appropriate nanostructuring of the “nanobubbles”. Experiments to demonstrate this potential are currently under way.

A Model for the Adsorption Kinetics of CO₂ on Amine-Impregnated Mesoporous Sorbents in the Presence of Water

Andrew Lee, David Mebane, David C. Miller, Dan Fauth, DOE/NETL, USA

A simple model for the adsorption kinetics carbon dioxide onto an amine-impregnated mesoporous sorbent, NETL-32D, was developed. The model was developed based on the mechanistic pathways believed to be responsible for the uptake of CO₂ by the sorbent, including interactions with H₂O. The model consists of quasi-ideal expressions to describe the kinetics of three reactions responsible for the uptake of CO₂ and H₂O by the sorbent. The model was fitted to experimental data obtained from thermogravimetric analysis and found to be a reasonable representation of the observed equilibrium and kinetics. The model is able to predict the increased uptake due to the interaction between CO₂ and H₂O in the sorbent. The heat of reaction predicted by the model for the uptake of CO₂ in dry conditions of -65 kJ/mol compares well to the value of -67 kJ/mol obtained via calorimetry for similar sorbents.

Investigation of High Temperature Steam Hydration of Calcium Oxide for Improved Carbon Dioxide Capture Over Multiple Cycles

Nihar Phalak, Niranjani Deshpande, L. S. Fan,
The Ohio State University, USA

Rising energy demand coupled with need to curb anthropogenic carbon dioxide (CO₂) emissions has led to the development of several clean coal technologies. The use of calcium sorbents for high temperature CO₂ capture has been widely investigated for such applications. In a typical process involving calcium sorbents, the CO₂ reacts with calcium oxide (CaO) in a 'carbonator' and the resulting calcium carbonate (CaCO₃) is decomposed to form CaO and a sequestration-ready CO₂ stream in a 'calciner'. The CO₂ capture capacity of CaO decreases over multiple cycles due to sintering during calcination and to overcome this problem, several techniques like physical and chemical modification of sorbents, preheating and grinding, etc. have been investigated. However, intermediate hydration of CaO seems to be the most practical and promising approach.

Hydration of CaO can be accomplished using water at ambient temperature or steam at high temperature. Our previous studies have revealed that water hydration results in superior performance of CaO toward CO₂ capture. However, operating the 'hydrator' at higher temperatures (400-600°C) using steam offers two distinct advantages. First, the high quality heat from the exothermic hydration can be utilized in heat integration. Secondly, since the calciner (850-1100°C) and carbonator (500-700°C) operate at a high temperature, the need for cooling and reheating the sorbent in each cycle is obviated. Hence, this study investigates high temperature steam hydration of CaO.

The feedstock for a calcium-based CO₂ capture system is limestone that is naturally occurring and abundant. Limestones vary in composition with geographical location and hence it is important to study different stones. The reactions occurring in each step of the capture process are likely to depend on the quantity of inerts and sorbent activity and this affects the mass and energy balances of the process. Six different naturally-occurring calcium sorbents have been evaluated at laboratory-scale over multiple carbonation-calcination-hydration cycles at high temperature and these results will be presented. Surface analysis techniques have also been applied to evaluate the impacts of pore volume and surface area on sorbent activity and the best-performing sorbent has been chosen for further study.

SESSION 5 Combustion: Emission Controls

Deactivation of Selective Catalytic Reduction (SCR) Catalyst by Phosphorus: Proposed Mechanism and Solution

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Selective catalytic reduction (SCR) is a commonly used technology for post-combustion nitrogen oxides (NO_x) emission compliance. One of the important co-benefits of the SCR catalyst is simultaneous mercury oxidation along with NO_x reduction. The oxidized mercury can then be captured in downstream wet or dry scrubbers. Exposure of SCR catalyst to coal combustion flue gas results in the deactivation of catalyst. Air staged combustion is another very common technique used to lower NO_x formation during coal combustion. Utilities firing Powder River Basin (PRB) coal with air staged combustion have been experiencing rapid deactivation of SCR catalyst. Utilities firing PRB coal with un-staged combustion have not experienced rapid deactivation. The rapid catalyst deactivation is believed to be primarily caused by gas-phase phosphorus (P).

The investigation of this problem by Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) began with field sampling of fly ash at utilities experiencing rapid catalyst deactivation. Size-separated fly ash samples were subjected to leaching tests to determine leachability of particulate-bound phosphorus. The leaching tests were conducted at pH level of 5, 7 and 9. Leaching studies ruled out particulate-bound phosphorus as the source of rapid deactivation.

B&W PGG modified the existing gas-phase phosphorus sampling method to reliably measure gas-phase phosphorus at high dust locations such as the SCR inlet. This modified method confirmed the presence of high gas-phase phosphorus concentrations at the SCR inlet of staged PRB units. Analysis of deactivated SCR catalyst logs showed the presence of vanadium-phosphorus bonds indicating a chemical deactivation occurs due to the interaction of gas-phase phosphorus with vanadium that is present in the SCR catalyst. It was also observed that the staged combustion process was contributing to release of gas-phase phosphorus due to carbothermic reduction of phosphorus-bearing minerals. A novel combustion additive and method was developed to tie up the gas-phase phosphorus before the SCR catalyst to reduce the rate of catalyst deactivation. A short-term proof of concept test was conducted at Wygen II power plant located in Gillette, Wyoming, to demonstrate reduction in gas-phase phosphorus due to the injection of combustion additive. Long-term additive testing has been proceeding at Wygen II since March 2010.

In this paper, we will present the results of long-term combustion additive injection testing to demonstrate reduction in the rate of catalyst deactivation and thus, improvement in SCR catalyst life using B&W's patent-pending combustion additive as

compared to earlier experience. Results will also be presented for simultaneous phosphorus mitigation and mercury oxidation using a blended combustion additive.

Development of Repetitive Pulsed Electron Beam Technology for Removing NO_x and SO_x from Flue Gas

John D. Sethian, Matt Wolford, Laser Plasma Branch, Naval Research Laboratory, USA

Electron beams have been demonstrated to remove, with a single flow through process up to 98% of the SO_x and 90% of the NO_x emissions from a coal fired power plant. The very efficient removal of SO_x allows use of lower cost high sulfur content coal. The process is well understood: ammonia and water are injected into the exhaust gas before irradiation. The electron beam dissociates the ammonia molecules into free radicals, which then reacts with the SO_x and NO_x to produce ammonium sulfate [(NH₄)₂SO₄] and ammonium nitrate [NH₄NO₃] fertilizer material. The quality of the fertilizer has been verified. This process has been demonstrated in small scale (~880 MW) pilot coal plants in the US, Japan, Germany, Poland, China, and Russia, as well as on oil based plants. The power to drive the electron beams is approximately 2% of the boiler power. (as a side note, there are also laboratory experiments that electron beams help in mercury removal by enhancing the oxidation efficiency--but this has not been demonstrated on a large scale.)

However the use of electron beams to clean NO_x and SO_x has not been adopted widely, primarily because of the expense. A large part of that expense may have been precipitated by the universal choice of a continuous electron beam source over pulsed source. A pulsed source, in which the electron beam duration is only a few hundred nanosecond (e.g. 100 millionths of a second) is projected to be 15-20 times more efficient for flue gas cleanup than a continuous system: This is because the electron beam turns "off" after dissociating the ammonia molecules, and thus does not inhibit the subsequent reactions between the resulting free radicals and the SO_x and NO_x. A pulsed source can also achieve the high instantaneous powers required for efficiently dissociating the SO_x and NO_x. A pulsed source is also expected to be less expensive as it only needs to withstand the high voltage at the output, and only for the duration of the 100 nanosecond duration of the pulse. Thus the system can be smaller and hence less costly.

Despite these anticipated advantages in efficiency and cost, continuous beam sources have been chosen because the technology did not exist to build viable pulsed systems. However recent advances in the Electra Program at the Naval Research Laboratory warrant revisiting the use of a pulsed system. Electra is part of NRL's program to develop the science and technology needed for an energy source based on inertial fusion energy. The Electra program has shown the way to a practical, efficient, and durable electron beam system with the proper parameters for flue gas clean up. Electra runs at up to 5 five times per second and produces a 500,000 Volt, 100,000 amp, 100 nsec long electron beam, of dimensions 30 cm x 100 cm. The voltage, integrated power, peak power, pulse length and electron beam size is very close to what is required for a flue gas system. The projected overall efficiency from, wall plug to electron beam energy deposited into the gas, is predicted to be greater than 65%. With relatively modest further development, Electra could provide the science and technology basis needed to transform this into a potentially efficient and economical means to remove harmful emissions.

The talk will discuss the advantages of a pulsed system, the advances made in developing the technology needed for a durable and efficient system, the estimated costs for a full size electron beam system, and the development path required for the flue gas scrubbing application.

This work has been sponsored by the US Department of Energy.

Modeling Secondary Coal Pyrolysis and NO_x Release for Pulverized Coal Combustion

Dong Zeng, Alan N. Sayre, Shengteng Hu, Hamid Sarv,
Babcock & Wilcox, USA

Coal pyrolysis is the initial chemical reaction step during combustion or gasification processes. The secondary pyrolysis of volatile compounds, including coal tar and light gases, accounts for a great portion of soot formation and the subsequent heat release and pollutant formation. While coal primary pyrolysis has been extensively studied over the last few decades and several network models have successfully described this process, coal secondary pyrolysis is still not well understood and as such, it is generally oversimplified.

For this reason, Babcock & Wilcox (B&W) has been investigating coal secondary pyrolysis in order to develop a comprehensive mechanism for inclusion in predictive computational fluid dynamics and coal combustion models. To understand and precisely model the secondary coal pyrolysis process, a comprehensive experimental investigation and modeling study was carried out, and a secondary coal pyrolysis and soot formation model named Coal Percolation Devolatilization / Secondary (CPD/S) was developed. Similar to its predecessor CPD model, the CPD/S model uses rank-dependent coal structure information to model tar evolution with reactions to account for tar cracking and soot formation. The CPD/S model was implemented into B&W's proprietary CFD code COMOSM to predict soot formation and NO_x emissions during pulverized coal combustion. The enhanced COMO model was then applied to compare its prediction with the experimental measurements of gas and particle compositions of

two different US coals under staged combustion conditions in a pilot-scale pulverized coal combustor.

Prediction of Emissions and Performance of a 650 MW Coal-Fired Boiler Using CFD

Alejandro Posada, Ismail Celik, West Virginia University, DOE/NETL;
Benjamin Chorpeneing, DOE/NETL; Nathan Jakinovich, Detroit Edison Belle River Power Plant, USA

The operation of a 650 MW subcritical pulverized coal-fired boiler is simulated by using a commercial computational fluid dynamics code: Ansys-Fluent. The geometry and operating parameters used in the model are based on actual data from the Detroit Edison Belle River Power Plant, to the extent available. Different turbulence, combustion, discrete phase and radiation models have been used to determine variations in the predictions due to modeling. Two radiation models, namely P-1 and Discrete Ordinates, and four turbulence models, namely: standard-, realizable-, RNG-ke, and RSM, were assessed. Five different meshes with 0.7, 1.6, 2.1, 2.7 and 5.7 million tetrahedral cells have been generated and used for the grid convergence and uncertainty analysis study. As the number of cells increases, the mass-weighted average temperature at the outlet of the boiler converges to an asymptotic value which is taken as an indication of grid convergence. Additionally, two different wall discrete phase boundary conditions for particles were evaluated, namely: “reflect” and “trap”. Preliminary results indicate that the velocities and temperatures obtained with the Discrete Ordinates radiation model are somewhat higher than those obtained with the P-1 radiation model. Approximately 55% of the particles injected were trapped at the walls when evaluating the “trap” discrete phase boundary condition. There was not a significant difference in the temperature field calculated from using the “reflect” versus the “trap” discrete phase boundary conditions for particle-wall interaction. An assessment of modeling errors is performed to determine which turbulence model should be used.

This paper includes a comparison of model results to available boiler performance data. This is an initial step, in development of a baseline model, in an effort to use CFD to study the effects of nonuniform boiler conditions on CO₂ emissions.

Mercury Emission Control by Wet Scrubber with Super Static Mixer

Shinji Kambara, Hiroshi Moritomi, Gifu University; Eiichiro Makino, Sojitz Corporation; Hisao Kojima, Mu Company Ltd., JAPAN

In pulverized coal combustion, the volatility of mercury and its compounds are emitted during combustion. In general, emissions of mercury from coal combustion sources are approximately 20–50% elemental mercury (Hg⁰) and 50–80% divalent mercury (HgII), which may be predominantly HgCl₂. HgII is water-soluble and may be removed from the flue gas by wet FGDs and dry deposition close to combustion sources, while Hg⁰ is diffused in atmosphere because Hg⁰ has a high vapor pressure and low water-solubility. To reduce mercury levels in the environment and human exposure, the removal techniques are desired. The main objective of this work is to investigate the influence of oxidation and absorption conditions on mercury removal efficiency to establish effective measures for mercury removal. The wet scrubber employed in this study is a unique design having a static mixer stirring flue gas and solvent. In experiment, model gas mixtures (Hg⁰/O₂/N₂ system and Hg⁰/O₂/NO/N₂ system) were prepared at room temperature. The model gases were oxidized by ozone generated by atmospheric plasma before treatments by the wet scrubber. Elemental mercury was converted to HgO by reaction with ozone at room temperature, and above 99% Hg⁰ removal was attained by the wet scrubber. Simultaneously, removal of NO was examined as a multipollutant control technology. Nitrogen oxide in the model gas was converted to NO₂ by reaction with ozone, and about 90% NO removal was obtained by using the wet scrubber.

SESSION 6 Mining: General

The Corrosion Potential of Rock Bolts on Coal Mines

A.J.S. Spearing, K. Mondal, G. Bylapudi, J. Weber, Southern Illinois University Carbondale; J. Hirschi, Illinois Clean Coal Institute, USA

The US coal mining industry uses about 100 million rock anchors per year. Corrosion has been found to be an issue in Australian coal mines (Hebblewhite et al, 2003 and Villaescusa et al., 2007) where the problem has been well researched and stress corrosion has been found to be a significant cause of rock falls. Corrosion is also a major concern for underground civil construction in the US but has not been considered an issue or adequately researched in coal mines. Conditions are conducive to corrosion underground mainly because of water quality and humid conditions. There is a perception however that when bolts are fully grouted, adequate corrosion protection is offered to the steel. Research has shown that this is not necessarily the case due to the formation of micro-cracks as the resin sets and with subsequent rock movement shearing the resin column. The paper outlines a method to determine the

corrosion potential of bolts used in long term excavations and suggests ways to mitigate such effects, based on research conducted in the lab and on three mines.

Characterization of Coal and Quartz Dust from an Indiana Mine

Y. P. Chugh, K. Mondal, V.K. Kollipara, H. Gurley, D.D. Relangi, Southern Illinois University Carbondale; Joe Hirschi, Illinois Clean Coal Institute, USA

Coal and quartz dust characteristics are important for the development of engineering controls. Coal dust characteristics vary as a function of mine geographic location and data is limited. This paper presents wetting, physical and chemical characteristics of coal and quartz dust, with emphasis on wetting characteristics. Particle size distribution, mineralogical and elemental compositions were analyzed on both bulk and in-mine samples. Correlations between wetting characteristics and physical and chemical characteristics were considered.

This study has developed a data base on these characteristics for several mines in the Interior coal basin. Coal wettability may be affected by the composition of different minerals present, surface properties and also on physical properties such as specific gravity of particles. The authors think that absolute wettability may not be a concern but wettability rate may be a concern. Therefore, contact time between dust and the wetting agent is important. The characterization data obtained from this study can be utilized to develop engineering controls to minimize dust exposure in coal mines.

An Integrated Model for Predicting Atmospheric Status in a Sealed Mine Area

J.W.Cheng, Y. Luo, West Virginia University, USA

Methane and coal dust explosions are the most feared hazards in the coal industry worldwide. A majority of these explosions were originated from or around the sealed areas. According to statistics, nearly all coal mine explosions initially started with the ignition of combustible gases such as methane, carbon monoxide, etc. However, due to inaccessible to the sealed area, predicting the gas composition change pattern and determining the explosibility of the gas-air mixture in a sealed volume become a challenge for mining engineers. In this paper, the most important factors to control the atmosphere compositions in a sealed area have been in detail analyzed. Based on these considerations, a mathematical model is proposed to predict the compositions changes in a sealed volume. In additional, the modified Coward's method is developed to check the explosibility of mine atmosphere, and new defined safety factor can also easily help the users understand the mine atmospheric status. Finally, the application of the integrated computer model in managing the mine sealed atmosphere is also discussed.

Assessment of SIUC Engineered Cribs for Mine Support

Harrold Gurley, Y. P. Chugh, Southern Illinois University Carbondale; Joseph Hirschi, Illinois Clean Coal Institute, USA

The SIUC engineered wooden crib known as the “ATLAS” crib was developed as an improved supplemental standing roof support for underground mining applications. These cribs are lighter in weight, offer lower resistance to airflow, can be installed more efficiently, and have higher stiffness than the conventional cribs. Three ATLAS crib designs, ATLAS 100, 200, and 300 series, were developed with different load carrying capacities and stiffness characteristics. Over the last three years, ATLAS 100 and 300 cribs were tested as a supplemental roof support in room-and-pillar and longwall mining operations in cooperation with National Institute of Occupational Safety and Health (NIOSH).

Both ATLAS 100 and ATLAS 300 cribs have demonstrated good characteristics for longwall entry and room-and-pillar supplemental standing roof supports in limited field studies during commercial use. This paper summarizes different field demonstrations and the performance of the SIUC developed innovative support systems.

A Numerical Analysis of a Four-Way Coal Mine Intersection with Primary and Secondary Supports: Additional Analyses

Y. P. Chugh, Behrooz Abbasi, Southern Illinois University Carbondale; Joseph Hirschi, Illinois Clean Coal Institute, USA

This research develops an improved scientific understanding of stress distribution and instability around a 4-way coal mine intersection with and without primary and secondary supports. Three-dimensional finite element analyses were performed with estimated Hoek-Brown failure criterion parameters for different lithologies associated with the coal seam. Entry width and horizontal stress have a major influence on intersection stability. Pillar ribs across an intersection fail first and lead to progressive failure of immediate roof and floor layers. The failure of roof layers extends about 1.8m, representative of field observations. Coal ribs mostly fail due to tensile stress, while roof and floor strata fail due to shear stresses. Rib corners fail due to a combination of shear and tensile stresses. Primary roof bolt supports significantly improve stability, but are not adequate. A 5-bolt pattern around intersection corners, with 2.4 m long vertical, #7 rebar, pre-tensioned bolts appears best as secondary support. Sequence of mining seems can have a positive effect on mine intersection

stability. The ‘Star’ pattern of bolting typically used does not have a major effect on intersection stability.

SESSION 7
Major CCS Demonstration Projects:
Financial Risk Management Strategies for CCT

Project Financing & the Texas Clean Energy Project (TCEP)
Eric Redman, Summit Power Group Inc., USA

A large coal gasification project, TCEP went through many permutations in configuration and design. Ultimately, TCEP was designed as a “poly-gen” plant to produce electric power and urea, with ninety percent (90%) carbon capture and the CO₂ being used for enhanced oil recovery (EOR) in the Permian Basin of West Texas. Summit Power, the project developer, intended TCEP from the outset to be project financed using conventional equity and project debt from private capital markets. TCEP later obtained key financial support from the US Department of Energy. This presentation will explain why Summit chose to develop a carbon capture project, how the rigors of project financing impacted project design, how Summit selected the key technology providers and major contractors, the challenges Summit faced in negotiating the myriad off-take agreements and vendor contracts, and how Summit and its financial advisors approached the challenge of raising more than two billion dollars in total equity and debt financing in domestic and foreign capital markets.

Building an Organizational Risk Management Framework
Michael Sell, Global Association of Risk Professionals, USA

The Global Association of Risk professionals (GARP) is a professional membership association whose principal mission is to help educate the global risk management community primarily through professional risk management designation programs, education and training, media and events. In the areas of financial and energy risk management, GARP sets the global standard with the Financial Risk Manager (FRM[®]) and Energy Risk Professional (ERP[®]) designations.

Over the past several years we have observed several global crises across a wide range of industries, each clearly demonstrating the importance of sound risk management practices. Increased regulation designed to solve structural weaknesses in the aftermath of these events will likely only go so far. Of equal or greater importance is the implementation of an appropriate risk culture that addresses the unique risks inherent in every organization. We will outline a general framework for defining, managing and evaluating the risk management process in all organizations.

Investment and Risk Transfer in Energy Markets
Glen Swindle, Eleven Madison, USA

The set of drivers that can affect forward energy prices and, by extension, capital allocation for infrastructure development, can act on many time scales. Some are slow moving and somewhat predictable, such as impact of unconventional natural gas resources. Others are fast moving and unpredictable, as evidenced by the credit crisis and its dramatic impact on both energy consumption patterns and the regulatory framework governing risk transfer activities. We survey some of the recent challenges facing lenders and portfolio managers in energy, including the effects of dramatic structural drops in power demand and the current low-price regime of natural gas relative to other fuels such as coal and oil.

SESSION 8
Gasification: Economics

Cost Comparisons of Coal-Fired Power Plants with Carbon Capture
Norman Z. Shilling, GE Power & Water; James R. Y. Rawson, GE Global Research; Jeffrey S. Goldmeier, GE Energy, USA

Numerous engineering firms and government agencies have published reports that compare the cost of various types of coal-fired plants which might be used for Carbon Capture and Sequestration (CCS) projects. These process economic analyses compare the cost of different types of coal-fired plants coupled with facilities required to capture CO₂ for either geological storage or enhanced oil recovery (EOR). These latter facilities are commonly referred to as carbon capture plants. Unfortunately, many of these cost comparisons do not use the same set of performance standards for the different types of coal-fired and carbon capture plants. In addition, most of these cost comparisons do not factor in the impact of maturity of these technologies.

In order for these cost comparisons to be relevant for making commercial decisions, the different types of coal-fired power plants and carbon capture facilities should all meet the same set of performance standards. These cost comparisons should also take

into account the interdependence of the operation of these plants with the design and operations required to transport of CO₂ in a pipeline and injection of the CO₂ into a geological formation for either storage in a saline aquifer or use for EOR. In addition, these comparisons should account for the impact the maturity of the technology has upon the cost of these processes.

In order to assure that these cost comparisons are all based on the same design criteria, the more important performance standards and costing methods are identified and defined in the ensuing discussions.

Load-Following Control of an IGCC Plant with CO₂ Capture
Debangsu Bhattacharyya, Richard Turton, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

In this paper, a decentralized control strategy is considered for load-following control of an integrated gasification combined cycle (IGCC) plant with CO₂ capture without flaring the syngas. The control strategy considered is gas turbine (GT) lead with gasifier follow. In this strategy, the GT controls the power load by manipulating its firing rate while the slurry feed flow to the gasifier is manipulated to control the syngas pressure at the GT inlet. However, the syngas pressure control is an integrating process with significant time delay.

In this work, a modified proportional–integral–derivative (PID) control is considered for syngas pressure control given that conventional PID controllers show poor control performance for integrating processes with large time delays. The conventional PID control is augmented with an internal feedback loop. The P-controller used in this internal loop converts the integrating process to an open-loop stable process. The resulting second-order plus time delay model uses a PID controller where the tuning parameters are found by minimizing the integral time-weighted absolute error (ITAE) for disturbance rejection. A plant model with single integrator and time delay is identified by a P-control method. When a ramp change is introduced in the set-point of the load controller, the performance of both the load and pressure controllers with the modified PID control strategy is found to be superior to that using a traditional PID controller.

Economic Evaluation of the UCSRP-HP Process in IGCC Applications
S. James Zhou, Arun Basu, Ajay Makkuni, Howard Meyer, Gas Technology Institute, USA

Gas Technology Institute (GTI) has been working with the University of California, Berkeley, for further development of their UCSRP-HP (University of California Sulfur Recovery Process- High Pressure) technology for integrated multi-contaminant removal of hydrogen sulfide (H₂S), carbonyl sulfide (COS), ammonia (NH₃), chlorides and heavy metals present in coal-derived syngas. In the UCSRP-HP process, H₂S is converted into elemental sulfur at 120 to 150 °C and at any given syngas pressure. During this research, data critical to developing and evaluating UCSRP-HP technology for multi-contaminant removal from syngas derived from Illinois #6 coal were obtained.

An economic evaluation was performed that integrated the UCSRP-HP technology into a nominal 550 MWe Integrated Coal Gasification Combined Cycle (IGCC) facility gasifying Illinois coal. The results indicated that the cost of electricity (COE) could be reduced by about \$9.60/MWhr (9.3%) compared to conventional IGCC technology with carbon capture, transportation, and sequestration, estimated at \$103.00/MWhr by DOE. The COE saving is mainly derived from a reduction in the overall capital expenses of about \$123 MM (December 2006 dollars). The UCSRP-HP design emits about 22 lb/hr (74 tonne/year) less SO₂; reducing the emissions to near zero would increase the capital by about \$10 MM and have a minimal effect on the COE. With these promising results, the UCSRP-HP process design was further integrated with advanced H₂/CO₂ separation technologies. With LANL/SRI’s PBI membrane, UCSRP-HP decreased the COE from \$98.20 to \$94.70/MWhr. With GTI/PoroGen’s CarboLock membrane contactors, the COE decreased from \$93.40 to \$91.70/MWhr. While replacing Selexol[™] with the Advance H₂ Membrane decreased the COE with RTI Warm Gas Cleanup from \$101.60 to \$89.60/MWhr, substituting UCSRP-HP for RTI resulted in an \$88.80/MWhr COE.

The UCSRP-HP technology may offer significant economic advantages over competing multi-component cleanup technologies in monetizing high-sulfur coals (e.g., Illinois basin coals). GTI is exploring various options to demonstrate this technology in a pilot plant using actual syngas from a coal gasifier.

Exergy & Economic Analysis of an IGCC-CSS Power Plant using H₂ and O₂ Separation Membranes
Nicholas Siefert, Carnegie Mellon University, DOE/NETL; Dhruv Bhatnagar, Shawn Litster, Carnegie Mellon University, USA

We present results from an exergy and economic analysis for an integrated gasification combined cycle (IGCC) coal power plant with carbon capture and sequestration (CCS) using existing commercial technologies, with the exception of the following yet-to-be commercialized technologies: oxygen separation via ceramic membranes and hydrogen separation via palladium membranes. We compare the results from these analyses with prior results from the National Energy Technology Laboratory (NETL) [1-2], as well as with the NETL/CMU Integrated Environmental Control Model (IECM) [3].

Included in our analysis is a calculation of the exergy destruction in each of the major pieces of equipment. Using the cost estimates from the prior studies as well as expected cost estimates for the membrane separation-reactors, we calculate the levelized cost of electricity (LCOE). By also including an average selling price of base load electricity in the US, we calculate the internal rate of return on investment (IRR) for this IGCC-CCS power plant design. Using these cost & price estimates, we find that advanced IGCC-CCS power plant with O₂ and H₂ separation membranes can achieve a real, i.e. inflation-adjusted, IRR of 5.9%/yr if the CO₂ is stored in a saline aquifer and 10.4%/yr if the CO₂ is used for enhanced oil recovery.

[1] Gerdes, K., Grol, E., Keairns, D., and Newby, R., 2009, "Integrated Gasification Fuel Cell Performance and Cost Assessment: DOE/NETL-2009/1361."

[2] Grol, E., and Wimer, J., 2009, "Systems Analysis of an Integrated Gasification Fuel Cell Combined Cycle: DOE/NETL-40/080609."

[3] Rubin, E. S., Chen, C., and Rao, A. B., 2007, "Cost and performance of fossil fuel power plants with CO₂ capture and storage," *Energy Policy*, 35(9), pp. 4444-4454.

Polygeneration Added Value to Coal Gasification

Aleksander Sobolewski, Institute for Chemical Processing of Coal, POLAND

In the paper there is presented coal gasification process as a key component of polygeneration (combination of electricity, heat and chemicals production).

Coal gasification is an integral part of IGCC technology which makes possible to separate CO₂ in pre-processing system and further direct it to sequestration. Produced combustible gas (syngas) can be used not only to electricity production but also optionally to chemical synthesis (e.g. engine fuel, methanol, urea and its derivatives so called "products trees"). In these processes occur so called chemical CO₂ sequestrations.

In the paper there is proved that variant polygeneration where exist combination of coal gasification and further synthesis gas processing increases economical process efficiency as well as production flexibility of whole production complex in market fluctuations.

Analysis was carried out on the basis of power plant of 309 MW_{el} connected with methanol production plant (550 000 mt/y) for site conditions of chemical company ZAK PLC (Kedzierzyn-Kozle, Poland) - one of the biggest European fertilizers producer. The plant processes annually ca. 2 mln mt of hard coal producing 1.55 bn Nm³ of syngas.

It was paid attention to fact that for present CO₂ emission limitation and functioning ETS (Emission Trading System) presented polygeneration plant allows to noticeable decrease total CO₂ reported emission for unit electricity production. Emission decrease can be achieved in proposed solution by:

- part of CO₂ chemical sequestration in the form of chemical products (in presented example it is 26% for methanol synthesis)
- input to gasification process of additional biomass stream substituting hard coal part (biomass in amount of 10% of total fuel chemical enthalpy)
- input (recycling) part of CO₂ stream separated from syngas to gasification reactor as a additional carbon source.

All presented and discussed options allow to noticeable improve economical efficiency of polygeneration plant and they make up interesting alternative for CO₂ geological storage.

SESSION 9 Coal-Derived Products: General – 2

Direct Hydrogen Production from Warm Coal and Biomass Syngas

Liyu Li, Chris J. Howard, Baowei Chen, Shari X. Li, Haobo Chen, David L. King, Pacific Northwest National Laboratory; Yuhua Duan, James C. Fisher II, DOE/NETL; Keling Zhang, Prabhakar Singh, University of Connecticut, USA; Yunhan Xiao, Research Center for Clean Energy and Power of Chinese Academy of Sciences, CHINA

The syngas from coal/biomass has many applications in the area of catalytic fuels and chemicals synthesis, and in the area of pure hydrogen production for petroleum refineries, ammonia synthesis and for fuel cell applications. In all cases, the gasifier-derived syngas must be treated to remove a number of impurities which would otherwise poison the processing catalysts. These impurities include alkali salts, chloride, sulfur compounds, heavy metals, ammonia, and various P, As, Sb, and Se-containing compounds. Many of these must be removed to part per billion levels due to their strong interaction with water-gas-shift and synthesis catalysts. Although technical approaches currently exist for removal of the contaminant species, they are rather costly, employing solvents at ambient or lower temperature. The efficiency of hydrogen production would be significantly improved if all the contaminants could be removed at temperatures higher than those for the low temperature water-gas-shift reactions (greater than 200°C). Also, after water-gas-shift reactions, the hydrogen product generated from coal/biomass syngas contains significant amount of CO₂, which also needs to be removed. Conventionally, CO₂ removal from H₂ stream also requires low temperature solvent-based operations, or low-temperature pressure-swing

absorption operations. The widely proposed absorption-enhanced reforming (AER) hydrogen production process, which combines hydrocarbon reforming, high temperature and low temperature water gas shift reactions and CO₂ removal into one single operation unit, can significantly simplify current multi-step hydrogen production technologies. Accordingly, by using a water-gas-shift catalyst mixed with a CO₂ absorbent, it is also possible to produce high purity hydrogen directly from clean warm coal or biomass syngases. High concentration CO₂ stream removed from syngases can be long-term stored, which can mitigate the biggest environmental problem of current world - global warming.

In this presentation, we will describe our recent joint progress in developing an integrated process for overall impurity and CO₂ removal and direct hydrogen production from coal and biomass warm syngases. This process consists of four major units: (1) A Na₂CO₃ absorption bed to remove HCl. At 450°C, Na₂CO₃ absorbent can remove HCl in syngas from 100 ppm down to less than 1 ppm, with 50 wt% capacity. (2) Two sequential ZnO beds to remove sulfur from >1000 ppm to <0.1 ppm: the upstream one as a regenerable bed for bulk sulfur removal and the downstream one as a high capacity sulfur polisher. (3) A metal-based absorption bed to capture low ppm level of sulfur, AsH₃, PH₃, and other trace-level contaminants. (4) A water-gas-shift catalyst loaded regenerable metal oxide-based CO₂ absorbents to capture and release CO₂ from warm gas streams (~400 °C) and to directly produce pure hydrogen. By using this novel process, we expect that the efficiency of hydrogen production from coal and biomass can be largely improved.

Catalytic CO₂ Char Gasification for Commercial Materials Production

Hua Song, Jason Trembly, Nandita Akunuri, Brian S. Turk, Raghubir P. Gupta, RTI International, USA

Our novel catalytic gasification process, which converts low rank coal char and carbon dioxide (CO₂) into valuable chemicals, uses the exothermic heat from partial oxidation of carbon to drive the endothermic reduction of CO₂. To effectively sequence the partial oxidation and reduction reactions and manage the heat needs across the reactor, a circulating fluid bed (CFB) reactor is used to move catalyst through the reactor. With this CFB design, optimal mixing of the catalyst, char reactant, and other gas phase reactants and highly efficient heat transfer and control are achieved in a compact footprint. Another unique feature of this reactor design is the ability to continuously add the solid char reactant. Furthermore, as the carbon in the char reactant is consumed, the size of the char particle decreases enabling effective separation of consumed char material from both the circulating catalyst and the gas phase product by means of cyclones or electrostatic precipitators (ESPs). The primary components in the product gas are carbon monoxide (CO) and CO₂. The CO₂ can be easily separate using conventional commercial technologies and recycled. The CO product can be used as a building block for a wide variety of chemicals and fuels

The catalyst plays a key role in successful operation of our process. Critical properties that this catalyst must have to ensure the success of this process include high activity for reduction of CO₂ and partial oxidation, high attrition resistance, tolerance to impurities introduced during gasification of the char such as H₂S, and low cost. To support development of catalytic activity for CO₂ reduction, intensive characterization of different catalysts and char samples at their different reaction stages using N₂ physisorption, pulse chemisorption, thermogravimetric analysis (TGA), temperature programmed desorption (TPD), temperature programmed reaction (TPRxn), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), x-ray diffraction (XRD), and transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS) have been performed to derive reaction mechanisms for the desired reduction reaction and competing or deactivation reactions.

Testing of the reaction between catalyst and char mixtures to provide data for deriving the reaction mechanisms has been conducted in a bench-scale fluidized bed reactor system. In addition to development of reaction mechanisms, this bench-scale reactor system has been used to complete parametric testing of operating conditions, which include temperature, pressure, gas space velocity, and O₂ concentration, to maximized CO production.

An integrated Aspen Plus® model of our novel catalytic gasification process, coal pyrolysis, and downstream processing of the product gas has been developed and used to generate a sized equipment list. With this sized equipment list, estimated capital cost and operating cost for a plant have been developed using factored estimating techniques. These cost estimates show a production cost of under \$18/ MM Btu for 99.99% CO assuming a \$10/metric ton of CO₂. Compared to the current quoted price for CO of \$35/ MM Btu, our process offers significant economic incentive. Additional sensitivity analysis has been used to focus research on development with the most economic benefit.

Determination of the Effect of Coal/Biomass-Derived Syngas Contaminants on the Performance of Fischer-Tropsch and Water-Gas-Shift Catalysts

Jason Trembly, Justin Farmer, Brian S. Turk, Raghubir P. Gupta, RTI International, USA

Today, nearly all liquid fuels and commodity chemicals are produced from non-renewable resources such as crude oil and natural gas. Due to increasing scrutiny of CO₂ emissions produced using traditional fossil-fuel resources, the utilization of

alternative feedstocks for the production of power, hydrogen, value-added chemicals, and high-quality hydrocarbon fuels such as diesel and substitute natural gas (SNG) is critical to meeting the rapidly growing energy needs of modern society. Coal and biomass are particularly attractive as alternative feedstocks due to the abundant reserves of these resources worldwide. The strategy of co-gasification of coal/biomass (CB) mixtures to produce syngas for synthesis of Fischer-Tropsch (FT) fuels offers distinct advantages over gasification of either coal or biomass alone. Co-feeding coal with biomass offers the opportunity to exploit economies of scale that are difficult to achieve in biomass gasification, while the addition of biomass to the gasifier feed leverages proven coal gasification technology and allows CO₂ credit benefits.

Syngas generated from biomass/coal mixtures will have a unique contaminant composition, because different gasification technologies are used to derive syngas from coal/biomass mixtures and coal and biomass possess different concentrations and types of contaminants. Syngas cleanup for gasification of biomass/coal mixtures will need to address this unique contaminant composition to support downstream processing and equipment.

To establish syngas specifications for utilization of gasification of biomass/coal mixtures for the production of transport fuels using FT synthesis, RTI has been testing commercial formulations of water-gas-shift catalysts (high temperature, low temperature and sour) and FT catalysts (cobalt- and iron-based) to investigate the effect of single components and synergistic effects resulting from multiple contaminants. Contaminants which have been investigated include NaCl, KCl, H₂S, COS, NH₃, and combinations thereof. This presentation will detail the individual and multi-contaminant experimental results from this testing program.

Effects of a Real Syngas on Pd-Alloy Hydrogen Separation Membranes

Bret H. Howard, Bryan D. Morreale, DOE/NETL; John M. Wheelton,
National Carbon Capture Center, USA

Gasification technologies are generally recognized as a viable near-term approach for addressing national fuel security and economic sustainability concerns, while simultaneously addressing the control of greenhouse gas emissions. The gasification process can utilize a variety of carbon-based feed stocks such as coal and biomass to produce a highly-flexible synthesis gas and, when combined with water-gas shift (WGS), can be effectively used to maximize hydrogen production. The hydrogen can be used for a variety of energy applications, including power generation via H₂ turbine combustion, power generation via fuel cell technologies and liquid fuels through several synthesis routes. Additionally, the integration of the water-gas shift reaction with simultaneous hydrogen separation (a WGS membrane reactor) can be used to enhance CO-conversion beyond that attainable in conventional reactors decreasing the necessity for multiple reactors, added catalysts, and large quantities of steam, while producing a highly concentrated, high pressure stream of carbon dioxide ready for co-sequestration. Dense metal membranes are a promising technology for the separation of hydrogen from these other product gases due to their high permeability and high selectivity for hydrogen. However, impurities typically contained in coal and biomass derived synthesis gas (compounds containing S, N, C, alkalis, heavy metals, etc.) can have adverse effects on metal-based separation membranes including corrosion and catalytic poisoning. Sulfur compounds, particularly hydrogen sulfide which can be present at concentrations as high as ~2% in a raw shifted coal-derived syngas stream down to low part-per-million levels following gas clean-up processes are probably the most detrimental to metal membrane technologies. H₂S is well known to severely impact the performance of dense metal membranes. These effects include catalytic poisoning and corrosion which can result in severe performance degradation and mechanical failure. In laboratory studies, the effects of minor contaminants such as As and Se compounds are not often considered. Therefore, developing a thorough understanding of the effects of syngas constituents, especially H₂S but including others, on metal membrane-based hydrogen separation membranes is imperative to facilitate the acceptance and deployment of membranes in gasification technologies.

NETL's Office of Research and Development is currently utilizing a variety of experimental and computational techniques to evaluate and develop potential sulfur tolerant membrane alloys. A variety of binary and ternary Pd-based alloys (Pd combined with Cu, Ag, Au, Pt, etc.) are being studied for application in the severe conditions and environments associated with the gasification process. Previously, the performance of these Pd-based alloy membranes were evaluated under laboratory conditions in the absence and presence of 1000 ppm H₂S in H₂ at conditions consistent with syngas processing. The observed hydrogen flux trends on exposure to 1000 ppm H₂S in H₂ were correlated with results obtained from post test XRD and SEM/EDS characterization. Recently, coupon samples of many of these alloys were exposed to actual syngas to evaluate their tolerance to real conditions. The coupon exposure was conducted in the Transport Gasifier at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. The coupons were exposed to syngas containing about 250 ppm H₂S for approximately five weeks at about 400°C for most of the exposure period. The post-exposure coupons were characterized by methods including x-ray diffraction and scanning electron microscopy to evaluate morphological changes and corrosion deposit formation. These results are compared to the performance data collected on the same alloys at NETL under similar controlled laboratory conditions. Preliminary examination of several of the membrane alloys indicates that the effects of actual syngas are, at least for some, different than observed under controlled, ideal conditions. In addition, effects of minor syngas components are reported. This experiment

represents a rare opportunity to study alloy performance under actual gasifier conditions and long exposure time.

Temperature Influence on the By-Products from Pyrolyses Processes of Coal and Comparison to the Theoretical Balance Model

Dagmar Juchelková, Veronika Sassmanová, Jaroslav Frantík, Stanislav Honus, Marek Večeř, VSB-Technical University of Ostrava,
CZECH REPUBLIC

The project concerns on the Technologies for pyrolyses processes and quality of fuels. We concern us also on the optimization of technology and the influencing of system and output parameters. According to the experiences of long term test form the small units was redesigned. The new unit allows making tests close to the real conditions. Some interesting information will be present.

SESSION 10

Carbon Management: CO₂ Capture - Sorbents - 2

Implications of Flue Gas Components on the Performance of Sorbent

James S. Hoffman, McMahan L. Gray, Daniel J. Fauth, Henry W. Pennline,
DOE/NETL, USA

Carbon sequestration is a viable scheme to mitigate carbon dioxide (CO₂) emissions from large point sources, such as power generators that burn fossil fuels. Although both the capture and storage steps are important, the most costly step is the capture one. The Fossil Energy Program in the U.S. Department of Energy has prompted the investigation of various techniques to capture carbon dioxide from coal-burning power generation point sources. A solid sorbent method, a category of post-combustion carbon capture, is a regenerable scheme where a solid material removes the CO₂ from the flue gas stream and is then regenerated. The technique can use an amine-based absorbent where the amine can be immobilized onto a support or encapsulated within a porous substrate. The sorbent becomes fully loaded once the CO₂ capacity of the sorbent is achieved. In a transport type of system, the spent sorbent is thermally regenerated in another vessel and recycled back to the absorption scrubbing unit.

With respect to CO₂ capture, loading capacity and regenerative heat duty are important parameters that define the technical/economic relevance of the sorbent. However, other components within the flue gas could have a direct impact on these parameters. The moisture of the flue gas can be important not only as it may be a reactant in certain CO₂-amine reactions, but by itself, it could possibly absorb onto the sorbent material, and thus cause an additional need for energy in the regeneration step. Depending on the requirement of upstream scrubbing of the flue gas in a flue gas desulfurization unit, the sorbent can be exposed to upwards of 15 vol% moisture in the flue gas. Additionally, if the flue gas emanates from the combustion of coal, it is eminent that the sorbent will need to contend with the trace gaseous components of sulfur dioxide and nitric oxides. Results of packed bed studies with an immobilized amine sorbent will be discussed. Gas mixtures simulated those of flue gas and the conditions for regeneration. The role of moisture in the absorption and regeneration steps will be described and its impact on CO₂ capacity and the regenerative heat duty will be addressed.

Modelling of Circulating Fluidised Beds for Post-Combustion Carbon Capture

Andrew Lee, David C. Miller, Larry Shadle, DOE/NETL, USA

A compartment based model for a circulating fluidized bed reactor has been developed based on experimental observations of riser hydrodynamics. The model uses a cluster based approach to describe the two-phase behavior of circulating fluidized beds. Fundamental mass balance equations have been derived to describe the movement of both gas and solids through the system. Additional work is being performed to develop the correlations required to describe the hydrodynamics of the system. Initial testing of the model with experimental data shows promising results and highlights the importance of including end effects within the model.

Efficient Theoretical Screening of Solid Sorbents for CO₂ Capture Applications

Yuhua Duan, Dan C. Sorescu, David Luebke, DOE/NETL, USA

Carbon dioxide is a major combustion product of coal, which once released into the air can contribute to global climate change. Current CO₂ capture technologies for power generation processes including amine solvents and CaO-based sorbent materials require very energy intensive regeneration steps which result in significantly decreased efficiency. Hence, there is a critical need for new materials that can capture and release CO₂ reversibly with acceptable energy costs if CO₂ is to be captured and sequestered economically. Inorganic sorbents are one such class of materials which typically capture CO₂ through the reversible formation of carbonates. By combining thermodynamic database mining with first principles density functional theory and

phonon lattice dynamics calculations, a theoretical screening methodology to identify the most promising CO₂ sorbent candidates from the vast array of possible solid materials has been proposed and validated. The *ab initio* thermodynamic technique has the advantage of identifying thermodynamic properties of CO₂ capture reactions without any experimental input beyond crystallographic structural information of the solid phases involved. For a given solid, the first step is to attempt to extract thermodynamic properties from thermodynamic databases and available literatures. If the thermodynamic properties of the compound of interest are unknown, an *ab initio* thermodynamic approach is used to calculate them. These properties expressed conveniently as chemical potentials and heat of reactions, either from databases or from calculations, are further used for computing the thermodynamic reaction equilibrium properties of the CO₂ adsorption/desorption cycle based on the chemical potential and heat of reaction. Only those solid materials for which lower capture energy costs are predicted at the desired process conditions are selected as CO₂ sorbent candidates and further considered for experimental validations. Solid sorbents containing alkali and alkaline earth metals have been reported in several previous studies to be good candidates for CO₂ sorbent applications due to their high CO₂ adsorption capacity at moderate working temperatures. In addition to introducing our selection process in this presentation, we will present our results for solid systems of alkali and alkaline metal oxides, hydroxides and carbonates/bicarbonates to validate our methodology. Additionally, applications of our computational method to mixed solid systems of Li₂O and SiO₂ with different mixing ratios, we showed that increasing the Li₂O/SiO₂ ratio in lithium silicates increases their corresponding turnover temperatures for CO₂ capture reactions. These theoretical predictions are in good agreement with available experimental findings.

Design and Characterization of Low Lifetime Cost Absorbents for Carbon Capture

Steven R. Lustig, Dennis Redder, Mark Scialdone, Ke Li, Hing Yim, Anne Marie Niehaus, Beth Cheney, Megan Quigley, Mark Shiflett, DuPont, USA

Enabling reduction of high volume CO₂ emissions from many existing commercial manufacturing and energy production plants requires substantial reduction of parasitic energy costs of carbon capture relative to known amine absorbent technologies. Design and realization of such efficient carbon capture processes must be based on low capital investment and operating costs over the process lifetime. The design and characterization of new CO₂ absorbents whose thermodynamic properties offer substantial reduction in capture process lifetime costs are described. Examples of leading liquid absorbents includes ionic liquids, vicinal diamine salts and thiones. Thermoeconomic modeling of the capture process readily quantifies the importance of key thermodynamic properties of the CO₂-absorbent system at operating conditions. Such key properties include equilibrium CO₂ solubilities, heats of CO₂-absorbent binding/release, and heat capacities of process streams. We present experimental measurements of all these properties using gas-liquid sorption studies and modulated differential scanning calorimetry. Our leading absorbents provide significantly reduced heats of binding/release and process stream heat capacities compared to aqueous monoethanolamine, which greatly reduces process lifetime operating costs. Our leading absorbents also require much lower desorption temperatures, which greatly reduces operating costs. Such improvements can also be realized with more neutral solutions and high sorption capacities, which reduces capital costs. In one example preliminary modeling indicates ionic liquid absorbent (*e.g.* 1-butyl-3-methylimidazolium acetate) can reduce energy penalty by 16%, investment by 11% and foot print by 12% compared with best known monoethanolamine technology. Experiments and modeling show further improvements possible using new absorbents (<\$60/mt) and the DOE goal (cost of electricity increase of no more than 35%) can be met.

Postcombustion CO₂ Capture Using Some Nanocomposite Amine Functionalized Sorbents

An Zhao, Arunkumar Samanta, Rajender Gupta, University of Alberta, CANADA

In this work, amine functionalized high surface area mesoporous silica sorbents have been prepared and tested at various CO₂ partial pressures using simulated flue gas to determine the adsorption capacity, regenerability, adsorption/desorption kinetics and multicycle durability of the sorbents. Functionalization of SBA-15 silicas with oligomeric amines, such as tetraethylenepentamine (TEPA) and polyethylenimine (PEI) has been achieved using the wet impregnation technique. The fresh, CO₂ loaded and regenerated adsorbent materials were characterized by small angle X-ray scattering (SAXS), nitrogen adsorption/desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectrometry. The CO₂ adsorption isotherms measured at four different temperatures (30, 50, 75 and 100 °C) by thermogravimetric method showed that the optimal adsorption temperature is 75 °C. The CO₂ sorption/desorption experiments performed at 75°C by thermogravimetric method revealed that CO₂ sorption capacities were about 4.02 mmol.g⁻¹ for the sample SBA-15/TEPA and about 2.81 mmol.g⁻¹ for the sample SBA-15/PEI. The CO₂ capture kinetics were found to be fast and reached 90% of the total capacities within the first 5 minutes. The textural properties of the raw materials and in particular, the mesopore contents seem to be the dominant factor for creating a

good dispersion of the amines into the pore channels of the silica support. Temperature-programmed desorption (TPD) of CO₂ showed that the desorption of CO₂ achieved maximal desorption rate at about 115°C and so is appropriate for thermal swing adsorption of CO₂ from flue gas. The cyclic CO₂ adsorption-desorption revealed that the TEPA impregnated SBA-15 sorbents exhibited good cyclic stability.

SESSION 11 Combustion: Oxy-Combustion – 1

Oxy-Fired Flue-Gas Recycle Pilot-Plant Demonstration

Thomas K. Gale, John T. Cover, Southern Research Institute; Timothy Fout, DOE/NETL, USA

A 1.0 MW thermal pilot-scale retrofit demonstration has been carried out in the Oxy-Fired Combustion Research Facility (OCRF) at Southern Research Institute, in Birmingham, AL. The pilot-scale facility, long used for research for the power industry, has been retrofitted to fire on pure oxygen and recycled flue gas taken from the stack. A carbon dioxide concentration of > 85% CO₂ in the flue gas has been achieved. The retrofit includes a completely new control system, burner management system, MAXON staged-oxygen burner, recycle fan, valves, and ductwork, and flue-gas cooler, mist eliminator, and scrubber cooler. The relevance and issues with each of the retrofit items above is explained as well as the relationship between the variable parameters of recycle percentage, oxygen staging, turn down, transition from air to oxygen and from natural gas to oxygen and coal. In addition, the results from similar testing on five different coal types are compared, including eastern and western bituminous coals and PRB sub-bituminous coal. This project was funded by USDOE National Energy Technology Laboratory's Innovations for Existing Plants Program.

Effect of Pure O₂ Injection on Flame Stability in Co-Axial Oxy-Fuel Turbulent Diffusion Flames

Dadmehr Rezaei, Eric G. Eddings, Kerry E. Kelly, Jost O.L. Wendt, University of Utah, USA

Past research at the University of Utah described the effect of partial pressure of O₂ in primary stream under oxy-fuel conditions. The research was conducted in a 100kW pulverized coal test rig with a co-axial turbulent diffusion burner. Burner used in these studies consisted of two streams namely: 1) Primary stream 2) Secondary stream. Oxygen was mixed with CO₂ in the both streams in all the combustion operating conditions. In oxy-fuel combustion, Oxygen injection is an independent variable that can have impacts on the stability of flame. The configuration of the pure oxygen injection in burners has a big influence on the turbulent diffusion mixing and the ignition of coal. Previous researches have shown the importance of oxygen injection in the center of burners on flame stability; however, the details of aerodynamics of flame and turbulent mixing in this case are not well known. A burner was designed for this research which is equipped with an extra stream called oxygen lance. Oxygen lance provides pure oxygen injection. The purpose of this research described in this paper is namely:

- 1) To Explore the effect of pure oxygen injection on the flame stability and combustion of coal in oxy-coal combustion with zero oxygen in the primary stream.
- 2) To investigate the effect of oxygen lance configuration on the flame stability and stand-off distance
- 3) To research the effect of oxygen lance on flame length

This paper; therefore, researches the effects of partial pressure of O₂ in the oxygen lance on flame stability and ignition in oxy-coal, coaxial, turbulent diffusion flames. In this study we investigated the stand-off distance and flame length using the same photo-image methodology described in the previous research. Temperature profile and NO_x values are measured and collected during this test.

Idea for Use of ASU Waste Nitrogen for Coal Pre-Drying within Oxy-Fuel Power Unit

Marcin Liszka, Grzegorz Szapajko, Grzegorz T. Nowak, Silesian University of Technology, POLAND

The proposed idea for use of nitrogen as a drying agent in a contact-type coal dryer is dealing with an oxy-fuel power generation process, where large amounts of waste nitrogen are available. The nitrogen, which is co-produced with oxygen in an air separation unit (ASU), is traditionally vented to the atmosphere. The main feature of ASU-waste nitrogen is near zero moisture content at near ambient temperature. Such a gas has a much higher moisture absorption potential than ambient air, so the waste nitrogen may be effectively used as a drying medium at relatively low drying temperatures. On the other hand, the drying of coal, especially lignite, is of positive impact on the boiler efficiency as liquid water which is originally contained in raw coal

is removed before fuel enters the combustion chamber. Application of nitrogen as a drying agent reduces also the danger of fire and explosion within the dryer.

The main goal of the present paper is to evaluate thermodynamic efficiency benefits related to introduction of coal pre-drying into oxy-fuel, coal-fired power unit. Three cases have been formulated and analyzed. First case is a typical 1st generation oxy-fuel power unit fed by lignite without fuel pre-drying. The coal drying process is arranged then conventionally in coal mills where flue gas is used as a drying medium. The second analyzed plant is equipped in a contact-type coal dryer fed by preheated air including moisture at typical ambient level. The third case is based on the previous one, but the ambient air is replaced by dry nitrogen taken from ASU. Main design parameters of all analyzed plants (steam parameters, boiler configuration, CO₂ compression train, etc.) are the same, which enable to determine the change of the net plant efficiency caused by the coal pre-drying process, as well as by the nitrogen use instead of ambient air.

SESSION 12 Coal Science: Beneficiation

Fe-minerals and Multiple Implications in Coal Cleaning Rejects

Frans Waanders, North West University, SOUTH AFRICA; Luis F. O. Silva, Marcos L. S. Oliveira, Kátia da Boit, Catarinense Institut of Environmental Research and Human Development – IPADHC, BRAZIL

In the present investigation a study was undertaken to understand the origin of Fe-minerals presents in Brazilian coal mining and to understand the environmental implication and the chemical heterogeneity in the study area. Coal cleaning residue (CCR) samples rich in clays, quartz, sulphides, carbonates, sulphates, etc. were sampled from Lauro Muller, Urussanga, Treviso, Siderópolis and Criciúma cities in the Santa Catarina State and a total of 19 samples were collected and Mössbauer, XRD, SEM/EDX and TEM analyses were conducted on the samples.

The major Fe-minerals identified are represented by the major minerals chlorite, hematite, illite, jarosite, and pyrite, while the minor minerals include, ankerite, chalcopyrite, goethite, maghemite, magnetite, marcasite, melanterite, natrojarosite, oligonite, pyrrhotite, rozenite, schwertmannite, siderite and sideronatrile. Pyrite is relatively abundant in some cases, making up to around 10% of the mineral matter in several samples. The sulphates minerals such as jarosite and others, probably represent oxidation products of pyrite, developed during exposure or storage.

The Determination of Drying Properties of High Moistured Turkish Lignites

H. Dincer Atesok, G. Atesok, M. Ozer, O. Kangal, Istanbul Technical University, TURKEY

The southeast part of Turkey region has considerably amount of coal reserves. Most of these reserves are located in Adıyaman-Gölbaşı Region which has about 60 million tons of reserves and also its geological reserve is estimated as 150 million tons. However, these reserves have highly amount of moisture (50%). The evaluation of these coals after dewatering and drying should be conducted to contribute these resources to Turkey's economy. In this study, the representative coal sample was obtained from Adıyaman-Gölbaşı Region. It contains 2183 kcal/kg lower calorific value, 37.8% of moisture, 24% of ash, 25.66% of flying matter, 12.54% of fixed carbon and 1.22% of total sulfur. Physical and chemical analyses, determination of minerals and particle liberation sizes of these minerals were determined. Also, some drying experiments in fixed beds and rotary driers were performed in dependence of drying period, various particle sizes and temperatures. These experiments showed that a dried coal with the moisture content of 8% and 3350 kcal/kg lower calorific value was obtained at 150 °C in 21 minutes drying period by using rotary drier while the same moisture content was obtained in 30 minutes using by fixed bed drying system.

Single Particle Impact Breakage of Coal

Jacob Viljoen, Quentin P. Campbell, North- West University, SOUTH AFRICA

Due to the large effect that size degradation of coal has on the value and usability of coal, it was necessary to determine the effect of various factors on the breakage of coal.

A sample of South Africa Highveld coal was the basis of the investigation. It was sieved into four size fractions (6.7-9.5 mm; 13.2-19 mm; 26.5-37.5 mm; and 53-75 mm). Particles from each fraction were handpicked based on the particle shape and classified as flat, elongated and spherical- or cubic particles. Enough particles were selected to drop 20 particles of each shape and size from three heights (2m, 5m and 7m). These particles were then dropped from the designated height onto a two centimeter thick steel plate, while the event was recorded using high speed video camera to determine both the speed of impact, and the particle orientation during impact. The degradation products were then all collected and a t₁₀ value determined, as well as proximate data.

The data was fitted to a model modified by Shi & Kojovic (2007). While the data wasn't a perfect fit a new empirical model will be proposed. The trends in the data also showed that the orientation of a particle just before impact has an influence on the t₁₀ parameter, while the ash content showed an inverted exponential relationship when plotted against the t₁₀ parameters, it had very little influence on the model.

SESSION 13 Major CCS Demonstration Projects: Insurance and Risk Management Strategies for CCS

Risk Management and Insurance: A Utility Perspective on CCS Deployment

Gary O. Spitznogle, American Electric Power, USA

Identifying, quantifying, and minimizing risk are essential for broad-scale acceptance and deployment of CCS technology and are key fundamentals in developing the proper insurance strategy for such projects. Particularly with respect to the geosequestration elements, substantial data collection and analysis is a must. Each project is unique, based on heterogeneity of geology, but much can be learned from previous experiences and strategies. As a world leader in demonstrating CCS at a commercial power plant, AEP has considered these topics in depth and will share its perspectives and approach toward risk management and insurance.

The Insurance Industry Perspective: Characterizing, Evaluating and Insuring CCS Risk

Robert P. Hallenbeck, Jr., XL Insurance - Environmental, USA

- I. The Environmental Insurance Marketplace: where it came from, where it is now
- II. XL Insurance - Environmental: business profile, risk appetite
- III. Coal, Carbon and the Insurance Market: recent history, current profile
- IV. The Risk Management Process: how do we do our due diligence, what are the components of our risk characterization, how does that translate into insurance coverage
- V. The Legislative and Regulatory Sectors: how do they impact our business, what is our level of interaction, what should it be
- VI. Transferring Risk Today: what do we insure, what don't we insure
- VII. Transferring Risk Tomorrow: what might we insure in the future, what will be important to the CCS industry
- VIII. Finding a Common Solution: should the stakeholders - industry, government, insurance - pursue a more interactive dialogue?

Risk Management Approach to Coal Utilization

Bob Percopo, AIG Chartis, USA

This presentation will begin with a brief summary of coal as an energy source for transportation and power generation, including its role as a "base load" component and its position in the dispatch curve. A decision making process to protect assets from physical loss and/or damage will be discussed, as will liability implications. Relative to CCS: What is it? What are the associated risks? Is the solution more dangerous than the problem? Coal plants have gotten larger and more expensive over time. How have plant size and cost impacted insurable risk? How have federal policies impacted risk profiles? What is key to understanding new technologies and their impact on risk management? Potential opportunities will be discussed in terms of transaction universe expansion, possible pressure on rates, and coal-to-liquids implications on imported oil. Similarly, relevant challenges will be addressed, including technical capabilities in the face of new technologies, capacity limitations for single projects, and surety bonding implications for construction of mega-projects.

Managing the Risks Related to CCS

Hans A Bratfos, DNV, USA

DNV (Det Norske Veritas) is an independent foundation established in 1864 with the purpose of safeguarding life, property, and the environment. From originally being a Norwegian ship classification society DNV has developed into an international company of 9000 employees present in 100 countries assisting our clients in the energy and maritime industries to succeed by managing risks.

One of the large uncertainties concerning the future of the coal power industry is related to future regulations of CO₂ emissions. How should coal power companies shape their policies in times of economic uncertainties and shifting political winds which prevent regulators from putting their ambitions into force? This is about managing risk.

In DNV's opinion, a low carbon society will not be realized within a foreseeable future without a transition period where Clean Coal Technologies will play a major role. Managing risks in various forms will be crucial for successful implementation of Clean Coal Technologies, this being political risks, commercial risks or technical risks.

DNV has specifically taken initiatives to develop guidelines and recommend practices together with industry partners and regulators which target some of the challenges within the Carbon Capture and Storage (CCS) value chain: New CO₂ capture technologies are needed to reduce CAPEX and OPEX in this most costly intensive part of the value chain. How should the risk of implementing unproven technology be managed? DNV has developed a recommended practice for qualification of new CO₂ capture technologies.

Transportation of dense phase CO₂ by pipelines is nothing new, but there are issues that need attention to make it right. DNV has issued a recommended practice which amends the common pipeline design standards for Natural Gas.

Geological storage of CO₂ is a controversial topic - some claim it is risky, others that it is perfectly safe. What are the risk factors, and how should storage operators and regulators co-operate to ensure safe and sustainable storage of CO₂? DNV has issued a guideline providing a systematic approach to selection and qualification of sites and projects for CO₂ geological storage.

SESSION 14 Gasification: Modeling – 1

Pressurized Entrained Flow Coal Gasifier Performance: A Parametric Study

Kevin J. Whitty, Travis Waind, David R. Wagner, University of Utah, USA

The University of Utah has commissioned a semi-pilot scale pressurized, slurry-fed, oxygen-blown entrained flow coal gasifier with a typical feed rate of 1 ton coal/day and a maximum feed rate roughly twice this. As part of the commissioning program, the gasifier was operated under a wide range of conditions and with several different feedstocks including lignite, PRB, eastern and western bituminous coals and petcoke. Pressures ranged from 100 to 260 psi (7 to 18 atm), feed rates (fuel dry basis) varied from 0.5 to 1.0 ton/day and oxygen/fuel ratios were varied by a factor of two. Reactor temperature profiles, synthesis gas compositions and flowrates were recorded during steady-state operation. This paper describes the experience of the commissioning process for the various fuels and presents performance data for the different fuels under systematically varied conditions. Trends generally follow expected performance, with higher oxygen/fuel ratios and higher throughput (resulting in shorter residence time) resulting in poorer quality syngas. System balances for conversion analysis are also presented.

Experimental and Modeling Studies of Pressurized Coal Gasification Behaviour

Daniel G. Roberts, San Shwe Hla, David J Harris, AUSTRALIA; JS Ravichandra, Jayesh Jain, GE Global Research, INDIA; ian Fengguo, Lv Jing, GE Global Research, CHINA; Greg Laskowski, GE Global Research; Shi Shaoping, GE Energy Gasification, USA

This paper presents an experimental and modelling study of the gasification behaviour of two US coals. The coals have been studied under conditions relevant to entrained flow gasification, using a high pressure entrained flow reactor. Coal conversion behaviour was measured at 20 bar pressure and temperatures between 1100°C and 1300°C, using molar O:C ratios between 0.6 and 1.3. Residence times were varied between 0.6 and 2.7 seconds, allowing tests at a range of conversion levels.

Further measurements were made using one of these coals to study the reactivity of the chars formed to CO₂ and H₂O at 20 bar total pressure and temperatures between 1000 and 1300°C, also using the pressurized entrained flow reactor. Such unique measurements allow a detailed understanding of the gasification reactivity of chars made from these coal samples, and demonstrate the importance of the fundamentals of gasification to our understanding of coal behaviour under industrially-relevant conditions.

GE Global Research and GE-Energy have developed a series of fundamentally-based gasification kinetic submodels that are amenable for implementation in CFD models for full scale and canonical reactors. Data from literature and in-house experimental set ups are used in the calibration and validation of these sub-models. This paper presents a further validation of these submodels (in a CFD set up) using the high temperature, gasification data generated in this current work as part of a collaborative effort with CSIRO. This continuing validation study helps to identify areas of improvement in certain other aspects, highlighting the need to further validate kinetics submodels.

Steady-State Modeling of a Single-Stage, Downward-Firing, Entrained- Flow Gasifier

Job Kasule, Richard Turton, Debangsu Bhattacharyya, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

Coal-fired gasifiers are the centerpiece of integrated gasification combined cycle (IGCC) plants, and generate synthesis gas that is cleaned and sent to the gas turbine for power production. Recent studies have developed mathematical models to describe the physical and chemical processes taking place inside the gasifier. Such models range

from simple one-dimensional (1D) steady-state equilibrium models to sophisticated dynamic 3D computational fluid dynamics (CFD) models that describe coupled gas–solid hydrodynamics, heat and mass transfer, and reaction kinetics over the complex gasifier geometry. In this work, a 1D steady-state model of a single-stage, downward-firing, oxygen-blown, slurry-fed, entrained-flow gasifier has been developed for use in the context of IGCC process simulation.

In the current model, mass, momentum and energy balance equations for solid (char) and gas phases are considered. The model includes a number of heterogeneous and homogeneous chemical reactions along with devolatilization and drying of the slurry feed. The unreacted-core shrinking model is used for calculating the rates of the heterogeneous reactions. A detailed model of the radiative heat transfer has been developed considering interactions between all internal surfaces (side wall, top, and bottom surfaces) of the gasifier and the solids along with the interactions between the surfaces themselves. In addition, the model includes the heat loss from the gasifier wall to the environment. In slurry-fed gasifiers, recirculation near the inlet of the gasifier is promoted for rapid mixing of the slurry feed with a portion of the hot reaction products. This violent mixing results in a significant rise in temperature that helps in evaporating the water and devolatilizing the coal. The recirculation is achieved by appropriately designing the feed burner, and feeding the oxygen through a swirling annular injector. In the current model, a heuristic recirculation model has been developed and the conservation equations have been appropriately modified.

The model described above is formulated as a set of ordinary differential equations (ODEs) in Aspen Custom Modeler® (ACM). Using ACM, the ODEs are discretized resulting in a highly nonlinear system of algebraic equations which are then solved using a Newton-type method. The gasifier model is validated using data available from experimental studies and pilot plants.

In this paper, the 1D steady-state gasifier model has been used to perform a number of parametric studies that provide insight into gasifier performance as the inlet and operating conditions change. Species concentration profiles and temperature profiles of the gas and solid phases are presented. A radiant syngas cooler (RSC) Aspen Plus® model is included in the study and its exit stream composition is compared to available industrial data. The effect of coal feed type on composition is also presented.

Experimental Validation of Syngas Composition of an Entrained Flow Gasifier Model Under Different Operating Conditions

Arnab Roy, Srinath Ekkad, Uri Vandsburger, Virginia Tech, USA

A computational fluid dynamics (CFD) based model of a single stage, dry-feed, down-flow entrained flow gasifier is developed and the effect of oxygen (O₂)/coal and steam (H₂O)/coal feed ratios on syngas composition is investigated. The model is set up using a coupled Eulerian-Lagrangian technique, where the continuous fluid phase is modeled in Eulerian approach and the trajectory of the coal particle is calculated in Lagrangian frame. The two phases are coupled by appropriate source terms in the conservation equations. Global gas phase homogeneous reactions are implemented in species transport model and the Discrete Phase Model (DPM) is used to account for the devolatilization and heterogeneous char gasification reactions. Steady state model predictions of the effective syngas composition (CO+H₂) at different O₂/coal and H₂O/coal ratios are compared with benchmark experimental data from literature and found to be in good agreement within the error bounds of the experiment. Results show gasifier exit temperature with increase in O₂/coal ratio, whereas it is found to decrease with increase in H₂O/coal ratio. The species composition also has a similar trend where it can be observed that the amount of syngas production is lower with increase of steam feed rate than compared to increase in oxygen feed rate. This can be attributed to the effect of water gas shift reaction which promotes the formation of CO₂ at higher steam concentrations. The further decrease in syngas production with increase in O₂/coal feed ratio (greater than 1) is due to the increased burning rate of coal which in turn lowers the residence time as a result of excess of O₂ supply. The simulation also provides detailed information of temperature and species concentration distribution inside the gasifier which indicates the three different reaction zones for devolatilization, gasification and reduction. A validated set of parameters are thus obtained that can be employed to improve design conditions for experiment. The model validation also provides the basis to achieve further accuracy incorporating complex effects such as detailed reaction mechanisms and effect of ash deposition.

Using Fundamental Data to Model Entrained Flow Gasification: Impacts of Coal Type on Gasifier Performance

San Shwe Hla, Daniel Roberts, David Harris, CSIRO Energy Technology, AUSTRALIA

This paper presents the development of a coal gasification model which incorporates existing mechanistic models with some new knowledge of gasification reaction fundamentals. The gasification model incorporates results of recent experimental studies into the effects of pressure on volatile yield, coal-to-char transformations, and high pressure gas-char reaction kinetics. In this model, the char particles from parent coal are classified into three morphological groups and gasification rates are determined using a 'composite effectiveness factor' by taking into account proportion of each morphological group of chars.

This gasification model has been used as the basis of the development of a model of an entrained flow gasifier by adopting a simplified flow representation using ideal

chemical reactors which consist of two plug flow and two well stirred reactors. Whilst clearly a simplification of a complex entrained flow gasifier, it accounts for the three dimensional aspects of recirculation and mixing and allows rapid convergence as required for incorporation into an IGCC process model.

This model predicts carbon conversion, cold gas efficiency, gas composition, char structures (such as char particle density, diameter, surface area), and gas and solid surface temperature profiles along the gasifier for four different Australian coals. Model results are compared with experimental data from a recent pilot scale experimental campaign using a 5 MWth entrained flow gasifier. Model results are found to be in good agreement with the data obtained from the pilot scale tests. Oxygen-carbon stoichiometry has a strong impact on char conversion, cold gas efficiency (CGE) and product gas composition. Consistent with this and previous experimental work, it is found that maximum CGEs for the higher reactivity coals with relatively high volatile matter are achieved within a narrow range of O:C ratios between 1.05-1.13 whilst the least reactive coal achieves its maximum CGE value at a higher O:C ratios of 1.36. Importantly, the model is able to reflect the significant differences in gasification behaviour of the four coals, which is consistent with lab-scale and larger-scale investigations using these coals.

SESSION 15
Coal-Derived Products: General – 3

Upgrading of Low Grade Carbon Resources through Solvent Treatment to Produce Solid Fuels and Precursors for Chemicals and Materials

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The authors have recently presented a degradative solvent extraction method to upgrade and fractionate wide range of low-rank coals into several fractions respectively having rather similar physical and chemical properties without loss of heating value under rather mild condition. In this work eight types of low-rank coals (sub-bituminous coals and lignites), a peat, two types of biomasses and the model compounds of biomass (lignin, cellulose and hemicellulose) were upgraded and fractionated by a batch reactor at 350 °C using 1-methylnaphthalene (1-MN) as solvent. The moisture in the raw materials was completely removed without phase change. The carbon in the raw materials were recovered as residue fractions (insoluble in 1-MN at 350 °C, carbon yield: 3-50 wt%), deposit fractions (soluble at 350 °C but precipitated at room temperature in 1-MN, carbon yield: 1-14 wt%), soluble fractions (soluble in 1-MN at room temperature, carbon yield: 14-24 wt%), and liquid fractions (carbon yield < 20 wt%). The carbon yields were rather different, depending on the type of raw materials. However, more than 80% of carbon were recovered as solid fractions (residue, deposit and soluble) in general. Furthermore, the solubles and deposits were almost free from ash, and were respectively rather close to each other in elemental composition, chemical structure, molecular weight distribution, pyrolysis behavior, and softening/melting behavior, independent of the type of the raw materials. The carbon contents of solubles were surprisingly as large as 80.0 - 84.0 wt%, and the oxygen contents were as small as 6.5 - 12.5 wt% on daf sample basis. The carbon contents of deposits were 74.3 - 80.0 wt% and the oxygen contents were 12.4 - 18.7 wt% on daf sample basis. The solubles consisted of the lowest molecular weight components of the three solid fractions, and their molecular weight distributions had a peak at around 250. The molecular weight distributions of the deposits had a peak at around 500. The solubles and deposits respectively melted completely at around 100 °C and at around 250 °C lower than the temperature of the decomposition reaction starting. It was also found that the sum of the heating values of the fractions were not lost during the treatment compared with the heating values of their parent materials. So, the solubles and/or deposits obtained from wide range of low grade carbon resources can not only be subjected to the same subsequent upgrading processes but can also be used for the same purposes. The residue fractions can be used as solid fuels because of their high heating values and rather low moisture content. Thus, the proposed degradative solvent extraction method was found to be effective to convert wide range of low grade carbon resources into solid fuels having higher heating values and compounds having rather similar chemical and physical properties.

High Yield Coal and Biomass Liquefaction by Hydrolysis with CO₂ Capture

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For most of the twentieth century there have been numerous methods to convert coal to liquid. The three primary methods have been pyrolysis/carbonization, hydrogenation, and indirect gas-to-liquids (Fischer-Tropsch). These methods are typically energy intensive, multi-step, or economically inefficient. A new hydrolysis process will be presented to convert coal into synthetic crude, which could be the most economic route as it eliminates costly hydrogen production in coal liquefaction. It also converts lignin, cellulose and other biomass co-feed easily. The new liquefaction method involves the addition of a proprietary catalyst with water and autoclaved at 200 - 350°C to yield a

liquefied product that is soluble in tetrahydrofuran, which can be further processed into consumer products in a conventional refinery. The process, which can substitute water for an alcohol had been found to generate 95% liquid yield with a nearly pure recoverable carbon dioxide (CO₂) byproduct. Data analysis of this product from coal has shown an increase in hydrogen and carbon content with a decrease in sulfur, nitrogen, oxygen, and ash.

The process was discovered based on the understanding of feed structure at molecular levels, organo-chemical aspects, and reaction thermodynamics. The chemistry can be illustrated as coal plus water to make hydrocarbon and CO₂ in a single step. The reaction itself is thermodynamically unfavorable. The CO₂ byproduct has to be removed completely by a caustic solution that drives the equilibrium to the product. The CO₂ is then recovered as an almost pure byproduct without additional separation, and the used caustic can be reclaimed by commercial available processes such as electrolysis of brine.

Benefits

- Single-step process
- Variety of feedstocks
- Pure CO₂ by-product
- High yields
- No hydrogen required
- Energy efficient

Liquefaction of Lower Rank Coal Under Mild Condition and the Structure Characteristics of Corresponding Heavy Products

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The hydrogenation of coal under mild conditions is an important step for the stepwise coal liquefaction process. Clear understanding of the characteristics of the coal liquefaction under the mild condition and the structure properties of the corresponding heavy products is desired for development of the methods that may predict and control the extent of the process. The characteristics of hydro-liquefaction of three lower rank coals (one sub-bituminous coal and two lignite samples) under mild conditions (1-5MPa pressure and 250-450°C) were studied. The structure properties of the corresponding heavy products were investigated by means of GPC, FTIR, CWSFS and TPD/FID&FPD. The reaction temperature and the properties of solvent were found to be two crucial important factors. If these two factors are properly selected, it is possible to run the reaction under lower H₂ pressure or even inert gas pressure without use of expensive catalyst and to meet the requirements for the next step. It may be achieved that obtaining coal liquids and upgrading the gasification reactivity of the lower rank coal in the same time.

Coal Gasification with Methane Reforming: A Novel Environmentally Benign CTL Process

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Production of liquid fuels from domestic resources would provide the United States with considerably enhanced energy security. US petroleum reserves are estimated at 30.5 billion barrels, which correspond to 1.2 cubic miles of oil (CMO). The US has abundant coal and natural gas resources. Coal reserves are estimated at 107 billion tons of bituminous and anthracite coals, and 129 billion tons of low-rank coals. Together they are equivalent to 35 CMO of energy. Likewise, natural gas reserves are estimated at 273 trillion cubic feet (tcf), and an additional 862 tcf are deemed technically extractable from shale gas resources. Combined, they are equivalent to 7.4 CMO. The current coal-to-liquids (CTL) and gas-to-liquids (GTL) processes are uneconomical and environmentally damaging because they consume large quantities of water and emit large amounts of CO₂. The main reason these processes are expensive, with high capital costs (about \$70,000/daily bbl), is that the Fischer-Tropsch chemistry on which they are based converts only a small fraction of the carbon to liquid products in the desirable boiling point range.

In response to a DARPA solicitation for a scalable CTL process that produces JP-8 for less than \$3.00/gal at a capital cost of less than \$15,000/daily barrel capacity, SRI proposed a process wherein syngas from coal gasification is converted to methanol, which is then used to produce JP-8. The SRI process uses natural gas as the source of hydrogen and electricity to drive the process. Using natural gas (methane) instead of water as the source of hydrogen is advantageous, because methane conversion is less endothermic and therefore its use reduces the overall energy requirement for the CTL process. By co-gasifying natural gas with coal, we can easily get a CO/H₂ ratio of 1:2, which is ideal for methanol production, and when coupled with processes for methanol to olefin, and olefin to JP-8, this scheme converts all the carbon in coal and methane into the desired liquid products. The process intensification so afforded reduces the gasifier size, and thereby the capital expenses. Furthermore, the process would not have any CO₂ emissions in the production of fuel, nor would it consume any water. SRI demonstrated the feasibility of this novel CTL scheme that uses natural gas as the source of hydrogen and electricity to drive the gasification of coal to syngas. Our laboratory experiments focused the most critical element of the scheme, the gasifier.

We showed that by having steam and/hydrogen in the entrainment gas we can successfully blow coal into an entrained flow reactor without excessive sooting. We demonstrated that high levels of conversion of coal and methane could be achieved within the short residence time of an entrained gasifier as long as the gasifier was operated at about 1400°C. We also showed the production of CO and hydrogen in a ratio acceptable for downstream processing to methanol. We used Aspen modeling to show that when coupled with COTS or near-COTS processes for methanol to olefin, and olefin to JP-8, this scheme converts all the carbon in coal and methane into the desired liquid products. JP-8 can be produced at \$2.82/gallon using relatively expensive CO₂-free electricity (@ \$0.10/kWh). JP-8 could be produced at considerably lower cost if lower-priced electricity is available. A well-to-wheel analysis shows that the carbon footprint of diesel produced by this scheme (326 g-CO₂/mile) would be smaller than petroleum-derived diesel (389 g-CO₂/mile), but is less than half that of the FT-diesel (830 g-CO₂/mile). If bio-sourced natural gas is used in the process, the resulting diesel would have a carbon footprint of only 190 g-CO₂/mile, and thus qualify under the expanded Renewable Fuels Standard, RFS 2, of the Energy Independence and Security Act (EISA), 2007. The capital cost for the plant is estimated at \$32,000 per daily barrel, which is higher than the target set by DARPA (\$15,000 per daily barrel), but considerably less than conventional Fischer-Tropsch based CTL plants.

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SESSION 16

Carbon Management: CO₂ Capture - Sorbents – 3

Effect of Surface Functionality for CO₂ Adsorption in Microporous Carbon

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To mitigate and stabilize atmospheric CO₂ concentrations, alternate energy sources with zero carbon emissions offer ultimate solutions. However, technologies based on efficient and economic generation of electricity from non-carbon-based energy sources are still in development. Therefore, carbon capture combined with sequestration as an aspect of a greater portfolio of solutions to reducing CO₂ emissions in the near future. As one of the attractive options, CO₂ captured by carbon-based sorbents as well as CO₂ sequestration in unmineable coalbeds require a thorough understanding of the adsorption properties in microporous carbon materials. A major obstacle is insufficient understanding of the molecular-scale processes involving CO₂ adsorption on organic matter with chemical heterogeneities at pressures and temperatures of interest. Current fundamental investigations of gas adsorption onto functionalized carbon surfaces involve the characterization of carbon-based samples by experimental methods, understanding of electronic properties of functionalized carbon surfaces by density functional theory (DFT), and the thermodynamic property predictions using a Monte Carlo (MC) method within the Grand Canonical ensemble.

Complex pore structures not only for coals, but also for other carbon-based porous materials have frequently been modeled as a collection of independent, noninterconnected slit pores with smooth, homogeneous graphitic walls. Density functional theory (DFT) calculations with van der Waals-inclusive corrections have been performed to investigate the electronic properties of the graphitic surfaces and the adsorbed phase of molecular CO₂. With a Bader charge analysis, DFT investigations also assist in setting up models for the initial framework required to carry out statistical modeling. However, the agreement between the MC and experimental adsorption experiments often involve structurally and chemically heterogeneous systems. With the chemistry of the organic matrix unknown in the current systems it is crucial that the initial models for MC are as representative of the chemistry as possible. Within the complex heterogeneous structure of the organic matrices of coal and other carbon-based porous materials, there likely exists a combination of defect sites and dangling bonds. The presence of volatile components such as water vapor, methane, and nitrogen- and sulfur-containing compounds is also expected. Indeed, these defects and functional groups are expected to play a role in the adsorption mechanisms associated with CO₂ on these systems depending on the local temperature and pressure. For instance, if the temperature and pressure conditions favor surface-bound water or various forms of dissociated water (e.g., hydroxyl or carbonyl groups) at the surface, this may lead to complex CO₂-water-surface interactions. Rather than CO₂ interacting directly with a surface, it may interact indirectly via a shared proton. Preliminary investigations also reveal that oxygen-containing functional groups will act to enhance the CO₂-surface adsorption.

Grand canonical Monte Carlo (GCMC) is used to connect the electronic properties of the adsorbents/adsorbates with the macroscopic adsorption thermodynamic properties. Different potential models for the CO₂ molecule are adopted to calculate the interactions between fluid molecules and between fluid molecules and pore walls. The implementation of the GCMC method yields the adsorption isotherms of a given adsorbent-adsorbate interaction and the selectivity for multi-component systems at various temperature/pressure conditions. The effects of surface functionalities have been investigated and the pore size distribution (PSD) of several carbon-based

materials are determined by comparing the simulated adsorption isotherms with available experimental adsorption data.

Effect of Additives on the Decomposition of Calcium Carbonate for Enhanced Steam Reforming of Methane Sorbent Regeneration

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Studies have shown significant improvements to methane (CH₄) conversions and production of hydrogen (H₂) when CO₂ sorbents are incorporated into the methane reforming reaction. The deactivation of Ca-based sorbents is well known in the literature and many studies have been conducted investigating the phenomenon. It has been suggested that sintering at high temperature is the primary cause involved in the deactivation process. The effect of additives on the decomposition of calcium carbonate (CaCO₃) was evaluated using in situ infrared spectroscopy coupled with temperature-programmed desorption, Raman spectroscopy, thermogravimetric analysis, X-ray diffraction, and density functional theory. The incorporation of additives, NaOH, Mg(OH)₂, Ca(OH)₂, LiOH, and CaO significantly affect the decomposition temperature of CaCO₃. The spectroscopic studies indicate that the alkali metal hydroxides convert the carbonate species to one that decomposes at a lower temperature. The low temperature decomposition of carbonates as gaseous CO₂ eliminates the issues with high temperature sintering, decreases the energy requirement for calcination, and offers an approach for improved Ca-sorbent performance for the methane reforming reaction.

Mesoporous Silica Hybrid Adsorbents for CO₂ Capture By Vacuum Swing Adsorption

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The capture and geosequestration of CO₂ emissions from major point sources such as coal combustion power generators could reduce anthropogenic greenhouse gas emissions and so help to slow global warming. Amine materials such as polyethyleneimine (PEI) loaded onto mesoporous silicas can exhibit large, reversible, water tolerant, and highly selective CO₂ capacities and fast sorption kinetics and so can be considered in conjunction with Vacuum Swing Adsorption (VSA), Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA) processes as one approach to the selective capture of CO₂ from flue gas.

This study has investigated the suitability of a variety of PEI functionalized mesoporous silicas under conditions that simulate the vacuum swing adsorption (VSA) process. Investigations have been carried out at modestly elevated temperatures (75 to 115°C), both in the absence and presence of moisture (dry vs humid conditions). VSA conditions were simulated by a partial pressure swing in a combined thermogravimetric analyser/differential thermal analyser (TGA/DTA). The physicochemical properties of the adsorbents were evaluated by a range of techniques, including infrared (IR) spectroscopy, nitrogen sorption, helium pycnometry, and thermogravimetric analysis. Increasing the temperature was found to be beneficial for achieving reversible CO₂ adsorption/desorption with reasonable working capacities and rates. In humidified feed streams the CO₂ working capacities were reduced slightly at temperatures above 100°C.

The longer term stability of the adsorbents was considered by conducting cycling experiments and also by prolonged exposure of the adsorbents to anhydrous 15% CO₂/Ar or humidified (1% H₂O) 15% CO₂/Ar atmospheres. Under dry conditions, PEI adsorbents showed a gradual decrease in CO₂ adsorption-desorption capacity; however, under humid conditions this reduction in capacity was substantially reduced. The chemical changes which accompany deterioration in performance were investigated by FTIR and NMR techniques. The loss of capacity appears to be associated with the transformation of amines into ureas. Results indicate that even a small partial pressure of water in the feed gas serves to inhibit urea formation.

SESSION 17

Combustion: Oxy-Combustion – 2

Effects of Moisture on Char Burnout During Warm-Recycle Oxy-Coal Combustion

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Oxy-coal combustion is a viable technology for curtailing greenhouse gas emissions from coal-fired power plants. It is a process of burning coal with flue gas diluted oxygen. Depending on where the recycled flue gas (RFG) stream is extracted, different combustion characteristics can be expected. "Cold-recycle" and "warm-recycle" modes of oxy-coal combustion are two ways of operating a power plant largely dictated by the fuel sulfur content. Under the warm-recycle condition, the flue gas moisture is not removed from the secondary oxidant stream, and the overall moisture content inside the boiler under steady-state operating condition could reach 35 vol%.

The effect of the elevated moisture and CO₂ levels on char burnout is the main subject of this study.

Previously, char burnout was studied under cold-recycle oxy-coal combustion and air-firing conditions. It was concluded that char-CO₂ gasification reactions can play an important role in char burnout. This effect is dependent on both coal rank and combustion condition. Continuing investigation began with the study of the effect of H₂O-rich gas on char burnout under warm-recycle oxy-combustion conditions using a western sub-bituminous coal as compared to the cold-recycle oxy- and air-firing conditions. All three conditions were generated on a flat flame burner (FFB) facility in which gaseous fuel and oxidizer mix and burn rapidly above its surface to produce a high temperature, one-dimensional flame zone. By adjusting the gaseous feed (fuel type, relative flow rate and inert dilution ratio), desired flame environment (temperature, O₂/CO₂/H₂O levels, etc.) can be generated. The pulverized sub-bituminous coal and its respective char (derived under a hot and inert atmosphere) were fed separately into the flame zone with 4 vol% oxygen that simulated post-flame boiler environment. Char samples at different residence times were collected and their extent of burnout was determined using the ash tracer technique. An optical fiber based two-color pyrometer was used to simultaneously acquire single particle surface temperature and velocity data. Experimental results demonstrated that high CO₂ and H₂O levels under oxy-firing conditions affect char burnout in two ways. On one hand, the char-CO₂ and char-H₂O gasification reactions can enhance burnout through direct consumption of char. On the other hand, the endothermic nature of these reactions can lower the particle surface temperature and hence decrease the char oxidation rate, which in turn leads to lower char conversion. The dominance of either effect is dependent on the coal type and the firing conditions (gas temperature, species concentrations, etc.). Char burnout for the sub-bituminous coal in the low-moisture, cold-recycle condition was higher relative to air-firing operation due to the dominance of char gasification by CO₂. In contrast, char burnout under warm-recycle oxy-combustion was similar to that of air-firing, indicating that the anticipated char gasification enhancement was equally negated by a cooler particle temperature.

The work is accompanied by modeling activities where the char oxidation sub-model in B&W PGG's COMOSM CFD code is evaluated under the test conditions. Both mass release and particle temperature data are predicted using Field's char oxidation sub-model with gasification by both CO₂ and H₂O considered. New kinetic rate parameters are derived from the experimental results.

Combustion of Solid Fuels in High Pressure Oxy-gas Environments under Different Firing Scenarios

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Oxy-fired combustion has been identified as one of the promising technologies for CO₂ capture because it is capable of producing a concentrated CO₂ stream suitable for sequestration. The use of pressurized oxy-fired combustion leads to certain advantages including thermal efficiency gains and physical size reduction of the combustor and flue gas treatment equipment. High pressure oxy-fired (HiPrOx) combustion systems have been proposed for use in power generation applications which fire coal with either a wet or dry flue gas recycle stream as a method for temperature moderation. HiPrOx has also been proposed for direct contact steam generation (DCSG) for use in industrial applications such as heavy oil extraction with solid fuels such as petroleum coke or asphaltenes. These firing scenarios present unique operating conditions and chemical species concentrations that affect the combustion characteristics of solid fuel chars.

TGA experiments were performed to study the effects of steam on a Canadian highvolatile bituminous coal char's reactivity in an oxy-fuel (O₂/CO₂/H₂O) environment. It was found that under kinetically controlled conditions, the increased addition of steam led to a reduction in burning time and temperature. The findings may have resulted from the lower heat capacity and higher thermal conductivity of steam compared to CO₂. These results differed from the lower gas temperatures observed near the burner of a pilot scale plant using a wet primary gas recycle in another study. It was postulated that, the suppression of H[•] radical concentrations resulting from the presence of H₂O and CO₂ during homogeneous ignition may have a greater effect on combustion temperature than the higher thermal conductivity and lower heat capacity of H₂O present in the environments investigated in this study.

Kinetics Rate Parameters for an Extended Single-Film Char Consumption Model Proposed for CFD Simulations of Oxy-Combustion of Pulverized Coal

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Reliable results of CFD simulations of coal-fired oxy-combustion boilers require char burnout models more sophisticated than those currently used for conventional air-blown boiler. In oxy-fuel combustion with flue gas recirculation (FGR), as is commonly employed, char combustion occurs in the presence of elevated CO₂ levels and, frequently, elevated water vapor levels (when employing wet FGR). Furthermore, local oxygen concentrations can be quite high in the vicinity of oxygen injection lances. Although the suitability of single-film models (i.e. with a chemically "frozen" boundary layer) is questionable for these environments, we have implemented an extended single-film model that includes 1-step steam and CO₂ gasification reactions

in addition to the usual oxidation reaction to facilitate improvements of CFD codes for prediction of the char burnout process. If we ignore the gasification reactions, both single-film modeling and detailed modeling show a strong discrepancy with experimentally measured char combustion temperatures for N₂- and CO₂-dominated atmospheres with typical bulk oxygen concentrations. In contrast, including the gasification reactions with typical activation energies found in the literature yields predictions in much better agreement with the experimental data. Initial results suggest that a computationally inexpensive, extended single-film model may be a reliable option for modification of existing CFD codes. The study presented here includes additional experimental data for assessment of the predictive performance of these models. Specifically, we investigated a high-volatile bituminous coal (Utah Skyline) and a low-sulfur sub-bituminous coal (North Antelope), that were both converted to char separately in a drop-tube reactor prior to using in the flow reactor. This eliminates potential effects of differences in the volatiles burnout in different oxidation environments on the reactivity of the char particles. The generated char was sieved to 6 narrow size fractions between 50 and 150 μm to aid evaluation of size-dependence of the burning temperatures. The char consumption process was studied using a combustion-driven entrained flow reactor equipped with an optical particle-sizing pyrometer, enabling non-intrusive observation of individual char particles burning in isolation from each other. For the discussion of the predictive performance of the extended single-film model, size-resolved temperatures measured during char combustion in both N₂- and CO₂-dominated atmospheres with 11 – 35% free-stream O₂ and in N₂- dominated atmospheres with 35% O₂ and 8 – 20% H₂O are compared with model predictions.

Effect of Biomass Blending on Oxy-Fuel Coal Combustion

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Oxy-fuel combustion burns coal in O₂/CO₂ instead of air (O₂/N₂) in conventional combustion. The major driving force for developing this technology is that it generates a CO₂-enriched flue gas, which will facilitate CO₂ capture and sequestration. Co-firing coal with biomass could further reduce effective CO₂ emissions and utilize renewable energy resources. However, pilot and laboratory studies have shown that the different properties of CO₂ and N₂ can produce significant differences in oxy-fuel combustion compared to conventional air combustion. Understanding these differences in the combustion process is important for the development and deployment of oxy-fuel combustion technology.

The National Energy Technology Laboratory (NETL) has an oxy-fuel research program with research activities focused on oxy-fuel process simulation for flexible fuels including coals and blends of coal and biomass. This study aims at obtaining experimental data to develop and validate detailed kinetic models for use in process simulation of oxy-fuel systems including those using blends of coals and biomass. The present study examines the impact of biomass on coal combustion process in the gaseous environments of oxy-fuel and conventional air combustion. A Powder River Basin (PRB) sub-bituminous coal, yellow pine wood sawdust pellets, and coal blended with up to 20 weight percent of this wood have been studied using thermogravimetry to 1000°C. For devolatilization, the behavior of both coal and wood is essentially the same in CO₂ as in N₂. However, the volatile yields (total fuel weight loss) at 1000°C under CO₂ are higher than in N₂ due to char gasification by the CO₂. The onset temperature for devolatilization of wood is lower than that for coal and this difference is reflected in blends of wood and coal; however, this difference is not seen when devolatilization occurs concurrently with combustion. For combustion, the blending of wood had impacts on the burnouts and the final residues of the fuel in air and O₂.

Reactivity Comparison of German Lignite and Victorian Brown Coal Chars Under Oxy-Fuel Conditions

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Oxy-fuel combustion is a promising technology for achieving near-zero CO₂ emission from coal combustion. Char combustion is the controlling step in coal combustion. In this study, we compare the combustion behavior of a German lignite char and a Victorian brown coal char under oxyfuel conditions. Chars were prepared from a German lignite (Hambach) and a Victorian (Yallourn) brown coal in a drop-tube furnace (DTF) at 800 °C in pure CO₂ atmosphere at an estimated residence time of 2 seconds. Char reactivity was investigated by a Thermogravimetric Analyzer (TGA) in the temperature range of 200°C to 1000°C at heating rate from 5K/min to 20 K/min and O₂ concentration from 2% up to 50% v/v in CO₂.

Both burnout temperature and the peak temperature were serious to be affected by the heating rate and oxygen concentration. With increase in the heating rate, both burnout temperature and peak temperature was found to increase for the two chars. The activation energies were also determined and compared. Except at 20% carbon conversion, the activation energies of German char were found to be much lower than that of Yallourn char. For the German char, the highest reactivity is observed with 50% O₂ in the gas; however, at around 800 °C temperature, the highest reactivity is obtained when the O₂ level is at 5%. Moreover, for Yallourn char, the highest reactivity is obtained at 5% O₂, which is much higher (more than double) than that of German char.

Particulate Formation from Pulverized Coal under Oxy-fuel Combustion Conditions

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Aerosol particulates are one of a variety of products generated by coal combustion. Combustion conditions can affect the formation of aerosol particulates, specifically, size distribution, amount, and composition. Understanding the formation of fine particulates is important for predicting emissions and understanding potential deposition. Oxy-fuel coal combustion conditions provide exhaust gas with a high concentration of CO₂ versus CO₂/N₂ due to the recycled flue gas. The hypothesis is that this high CO₂ concentration reduces the vaporization of refractory oxides from combustion according to the reaction: MO_n(s) + CO(g) ↔ CO₂(g) + MO_{n-1}(g). This research investigated particulate formation in a drop tube furnace under different flue gas scenarios. Ash particulate formation has been studied as a function of furnace temperature, coal type, and gas phase conditions, namely, CO₂ versus N₂. A Scanning Mobility Particle Sizer (SMPS) and an Aerodynamic Particle Sizer (APS) were utilized for ash particle size distributions in sizes ranging from 14.3 nm to 20 microns. In addition, particles were collected on an eleven-stage, Berner Low Pressure Impactor (BLPI) for elemental analysis using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Ultra fine ash deposition was directly related to temperature, increasing with increasing temperature. The results showed a change of particle size for high calcium and silicon coals as hypothesized.

SESSION 18

Coal Science: Coal Geochemistry

Review of Minor Element Distribution in Iron Disulfides in Coal

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The iron (Fe) disulfides pyrite and marcasite are of primary interest to coal scientists, not only as contributors to sulfur emissions during coal combustion, but as hosts for inorganic minor constituents that are considered hazardous air pollutants. Electron probe microanalysis (EPMA) of numerous samples in USGS labs over nearly 15 years confirms that arsenic (As) is the most abundant and most commonly enriched minor constituent of pyrite in coal, with selenium (Se), nickel (Ni), cobalt (Co), copper (Cu), and zinc (Zn) less commonly enriched at lower levels. In most coals, multiple generations of Fe disulfides are present, and these may show grain-to-grain and within-grain compositional variation that is a function of the early diagenetic, coalification, and post-coalification history of the coal. Framboidal pyrite is always the earliest generation, as shown by overgrowths of later, commonly subhedral pyrite. Cleat- or vein pyrite is latest generation, as shown by cross-cutting relations with respect to earlier pyrite generations. Cleat- or vein pyrite forms by fluid migration within a coal basin and consequently, each may be enriched in elements such as As, especially where deposition from metal enriched hydrothermal fluids occurs. In several cases to be shown, framboidal pyrite shows preferential Ni enrichment with respect to co-occurring pyrite forms. This is consistent with bacterial complexing of metals during early diagenesis, and possibly, derivation of framboidal pyrite from greigite (Fe₃S₄), an iron monosulfide precursor having the spinel structure which accommodates transition metals. Metals such as Ni, Co, Cu, and Zn substitute for Fe in Fe disulfides whereas Se and metalloids such as As substitute for sulfur. Mercury (Hg) occurs in Fe disulfides at concentrations below detection by EPMA in nearly all cases but its presence is known empirically by other methods. Mercury likely substitutes for Fe, but its ionic state in Fe disulfides is poorly known. Understanding the distribution of minor and trace elements in Fe disulfides in coal has important implications for their potential reduction by coal preparation as well as delineating diagenetic compositional changes throughout and post-dating coal formation.

Development of an Improved CCSEM Technique for Quantitative Coal Mineralogy

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An improved approach for quantitative determination of coal mineralogy based on the recently introduced QEMSCAN technology is being developed. The QEMSCAN-based technique offers the ability to significantly increase the number of particles detected and analyzed and, hence, improves the statistical population of particles used to classify and quantify the mineralogy of the coal samples. This new approach also allows for a much larger number of particles to be analyzed in individual subpopulations, called size bins, which are used in the conventional computer-controlled scanning electron microscopy approach at the Energy & Environmental Research Center. As a result, the particle statistics for the individual size bins are also improved. Preliminary results show much promise and significant improvement in some cases, especially with regard to the determination of pyritic minerals and minerals rich in alkali and alkaline-earth elements of interest, such as Na, K, Ca, and Mg. These elements are known to play important roles in determining the behavior of North Dakota lignite during combustion and/or gasification with regard to slagging,

fouling, and corrosion characteristics, as well as impact selective catalytic reduction catalysts where applicable.

Geological Framework and Economic Potential of Newly Discovered Coal Prospect in Midwest Tenement, Moatize Coalfield, Tete Province, Mozambique

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A new economically important multi-seam coal prospect covering an area of 80 sq km is discovered in the northern segment of N.Kondrezi area of Moatize Basin of the Gondwanic Zambezi rift valley, Mozambique. The WNW-ESE trending trapezium shaped coal prospect exposes Permian sediments divisible into Dwyka, Productive and Matinde Formations in that order. The Productive Formation is now found to comprise three informal members namely the Lower Coking Coal Measures, Middle Barren Measures and Upper Thermal Coal Measures broadly correlatable to Barakar, Barren Measures and Raniganj Formations of the Indian Gondwana stratigraphic units. Structural framework of the coalfield is half graben transected by WNW-ESE longitudinal and NE-SW Transverse faults.

The Productive Formation is characterized by the presence of fining upward coal cyclothem made of sandstone, siltstone/shale and coal deposited in alluvial plain - coal swamp setting. Syn-sedimentational faulting controlled the sediment accumulation in the basin. Ten coal zones corresponding to ten prominent coal cyclothem are delineated. Each coal zone consists of alternating units of shale and coal beds and it is that go into making potentially workable coal sections. Coal is Bituminous, Vitrain rich, high in ash % but marked by high heat value. Coal from zones I to IV of Lower Coal Measures shows coking propensity indicating Prime to Semisoft grade, whereas the coal zone V to X of upper coal measures are of thermal grade. The hitherto carried out exploration brought to light a 3.6 to billion tonnes of JORC Inferred category coal resource with a potential prognostication uptrend to over six billion tonnes. Therefore, the present findings mark a distinct addition to Moatize Coalfield Resource inventory thereby opening up a new dimension to coal exploitation by the Midwest Coal company in Mozambique.

Although the Moatize coalfield holds coal potential to the tune of 20 billion tonnes, coal production is yet to commence on modern lines and therefore information available on Moatize Coal exploitation and utilization pattern has remained sketchy. The present communication incorporates salient aspects of coal quality and coal preparation with an intention that it sets tone for further research on coal utilization and related issues in Mozambique.

Analysis of Trace Hazardous Elements in Flue Gas Desulfurization Water and the Removal of These Elements from the Water

Akira Ohki, Tsunenori Nakajima, Hirokazu Takanashi, Kagoshima University, JAPAN

Several coals were tested in a pilot plant of coal combustion facility, and a slurry supernatant water from the wet flue gas desulfurization (FGD) system was obtained. The determination of trace elements in those FGD water samples was done by ICP-AES, ICP-MS, and other methods, while the analysis of major cations and anions was conducted by ICP-AES and ion chromatography, respectively. The levels of B, Se, and Hg in the FGD water samples sometimes exceeded the Japanese national effluent standards for terrestrial water (10, 0.1, and 0.005 mg/L for B, Se, and Hg, respectively). When oxy-fuel combustion was carried out by use of the same combustion facility, the concentrations of trace elements in the FGD water samples tended to be lower than those for the normal combustion. The removal of these hazardous trace elements was attempted by adsorption method and photocatalytic reduction method.

SESSION 19

Major CCS Demonstration Projects: General – 1

U.S. Department of Energy's Major Demonstration Program

Michael Knaggs, DOE/NETL, USA

The U.S. Department of Energy's (U.S. DOE's) Office of Fossil Energy (FE) and the National Energy Technology Laboratory (NETL) have a long history in financially supporting major demonstrations of advanced clean coal technologies. With the enactment of Public Law 99-190 in April 1985, the U.S. DOE embarked on its first of five solicitations under the Clean Coal Technology Development Program (CCTDP). The CCTDP resulted in thirty-three successful projects covering a range of technologies. Following the blackouts and brownouts of 1999 and 2000, the Congress created the Power Plant Improvement Initiative to seek significant improvements in power plant performance and reliability. In November 2001, the Congress passed Public Law 107-63 creating the Clean Coal Power Initiative (CCPI); thus far, projects from three solicitations have been supported. The American Recovery and Reinvestment Act of 2009, Public Law 111-5, not only provided

additional funding for the third CCPI solicitation, but it also created the Departments Industrial Carbon Capture and Sequestration (ICCS) program and provided funding for the FutureGen 2.0 project.

Today, current emphasis within FE's and NETL's Major Demonstrations Program is on the large-scale demonstration of advanced carbon capture technologies and the sequestration of carbon dioxide in geological formations, including its use for enhanced oil recovery. The objective of the current program is to demonstrate a suite of CCS technologies that minimally impact the cost of electricity and can be ready for commercial deployment by the end of this decade. The portfolio of proposed technologies for demonstration that are applicable to coal-fired utilities include post-combustion CCS, gasification with CCS, and oxy-combustion. Within the industrial sector, CCS will be demonstrated from steam-methane reforming, biomass fermentation, and gasification-based methanol synthesis. Although this presentation will provide a brief historical overview of NETL's major success from prior demonstration programs, emphasis will be on providing an overview of the status of the current slate of active commercial-scale projects.

Alberta's CCS Programs and the Role of New Technologies

Duke du Plessis, Alberta Innovates: Energy and Environment Solutions,
CANADA

Alberta is uniquely suited for CCS because of the proximity of large emitter point sources and CO₂ sinks in the Western Canadian Sedimentary Basin. Oil and gas reservoirs located kilometres deep underneath the earth's surface that have been depleted by conventional drilling can be used for storing CO₂. The Government of Alberta allocated \$2 billion for CCS demonstration projects as part of a long term green house gas management strategy. Four projects were selected following a thorough review of dozens of projects that had submitted Expressions of Interest and full project proposals. These projects are intended to capture 2.2 million tonnes per year of CO₂. The Alberta Carbon Trunk Line will be a 240 km CO₂ pipeline distribution system, capable of gathering CO₂ from several sources in the Alberta's Industrial Heartland and transporting the CO₂ to existing mature oil fields. The CO₂ will be captured from an existing fertilizer plant and a new bitumen upgrader/refinery. The Quest project will capture and store 1.2 million tonnes of CO₂ annually beginning in 2015 from Shell's Scotford upgrader. The CO₂ will be sequestered in a nearby geological formation. An in-situ coal gasification (ISCG) project will access deep coal seams to convert the coal underground into a clean synthetic gas that will be used for power generation. The CO₂ will be utilized for Enhanced Oil Recovery (EOR). Project Pioneer will utilize leading-edge technology to capture CO₂ from a stack gas slipstream of a new 300MW coal fired power plant. The CO₂ will be sequestered or used for EOR. The paper will summarize the status of these projects and describe other initiatives such as Alberta's Climate Change and Emissions Management Program which invests funds collected from large industrial emitters into the development and application of new and improved emission reduction technologies.

The Case for Carbon Capture & Storage (CCS) as a Clean Development Mechanism (CDM)

Steven M. Carpenter, Advanced Resources International, Inc., USA

The Carbon Capture & Sequestration (CCS) marketplace is lacking standardization and therefore the ability to allow CCS projects to be considered as Clean Development Mechanisms. There is an international push to change this and recognize CCS. This recognition will allow for standardized and ultimately address a much needed CDM option and international standardization.

This process is beginning with a bi-national effort between the United States and Canada. CSA Standards, a leading developer of standards, codes and personnel certification programs, and the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO₂ Research Inc.) have partnered to develop a bi-national American-Canadian carbon capture and storage (CCS) standard for the geologic storage of carbon dioxide (GSC).

The GSC standard will be developed by leading North American experts and, upon completion, will be the world's first formally recognized CCS standard in this area. It is intended that the new standard will be used as a basis for the promotion of international standards through the International Organization for Standardization.

The standard is expected to be completed by the end of 2011. CSA Standards will manage the standards development process through the establishment of a Technical Committee (Committee) that shall be responsible for developing and maintaining the standard. A seed document based on existing industry guidelines, related standards, and IPAC-CO₂ expertise has been prepared and will be presented to the Committee for consideration. The Committee, with process and editorial support from CSA Standards, will be completely responsible for the content of the final standard. Membership of the Committee will be drawn from experts with full GSC project life cycle knowledge and experience and will represent a balance of stakeholder needs.

The bi-national American-Canada Consensus Standard will address the full geological carbon dioxide storage project life cycle including: site selection, operation, closure, and post-closure stewardship. It is expected that ISO standardization and certification will follow. The presentation intends to provide an overview and discussion of the process from the perspective of a Technical Committee member (e.g. the Author).

Monitoring Large Volume of CO₂ Injection at Cranfield: Early Field Test of SECARB Phase III

Changbing Yang, Susan Hovorka, Gulf Coast Carbon Center, Bureau of
Economic Geology the University of Texas at Austin, USA

The early field project of the Southeast Regional Carbon Sequestration Partnership (SECARB) was conducted in a depleted oil and gas reservoir, Cranfield Field, western Mississippi. CO₂ injection started in July 2008 through ~23 wells with total injection rates greater than one million tons/year into coarse grained fluvial deposits of the Cretaceous lower Tuscaloosa formation in a gentle anticline at depths of 3300 m. Comprehensive monitoring programs of deep subsurface and near-surface have been implemented at different study areas for different purposes. Here we present the monitoring results at two areas: the Detailed Study of Area (DSA) and the P-site with Plants, Plugged & abandoned well, Pit, and Pad. At the DSA, intensive data including downhole and above-zone pressure, distributed temperature, fluid chemistry and tracers (perfluorocarbons, noble gases, and SF₆) have been collected at the DSA where one injector and two observation wells were heavily instrumented. Other geophysical approaches, such as electrical resistance tomography (ERT), time-lapse crosswell seismic, and time-lapse VSP were also used in this study for tracing CO₂ plume in the storage formation and providing data for numerical modeling. Detecting CO₂ potential leakage at the near-surface environments is complicated because of variability in natural CO₂ noises, as well as the past oil-production activities at typical sequestration sites. Goal of study at the P-site is to understand interactions of natural CO₂ sources with constructed features, including gravel well pads and pit excavations formerly used to handle drilling mud and further to demonstrate feasibility of monitoring soil gas chemistry for detecting CO₂ potential leakage. More than 20 soil gas wells instrumented with copper tubes at different depths were installed at a well pad along three cross-sections. Weather information and soil moisture contents of the P-site were automatically collected. Soil gases were sampled from the soil gas wells and analyzed using a gas chromatography on site. Data of shallow groundwater were also collected from 10 "make-up" wells for water chemistry monitoring.

This early field project is funded by the US Department of Energy, National Energy Technology Laboratory as part of the Regional Carbon Sequestration Partnerships program. SECARB is led by Southern States Energy Board.

SESSION 20 Gasification: Low Rank Coal

Coal Fired IGCC Power Plants in Wyoming

William C. Schaffers, David Bell, University of Wyoming, USA

Coal fired IGCC power plants may become an important source of electrical power generation if the regulation of CO₂ emissions becomes reality. The state of Wyoming would seem a likely location for such plants due to its abundant supply of inexpensive coal. The presence of oil and gas fields in the state would also provide a repository for the CO₂ with the added benefit of enhanced oil and gas recovery.

Numerous AspenPlus models were constructed to study different IGCC scenarios. These scenarios included Green River and Wyodak coals and two different gasifier configurations. Feed types studied were dry, slurry and inherent moisture without drying or slurrying. Carbon dioxide capture levels compared were 0%, 70% and 90%. In addition, several methods to reduce water requirements, including air cooling, were modeled. Net power generation, water requirements and economic factors were compared for the various models.

An Excel spreadsheet program was constructed for the economic analysis of the different AspenPlus scenarios. These spreadsheet models estimated capital and operating costs for the various plants. They also calculated the IRR for various electricity prices as well as the electricity price needed to obtain a 12% IRR. Analysis of the economic data included capital cost comparisons as well as IRR and electricity production cost comparisons for the different IGCC configurations.

It is hoped that the results of these studies can be used by corporations in conjunction with the state of Wyoming to help determine the most appropriate configuration for IGCC power plants located within Wyoming. These models should be beneficial to both the state and industry in utilizing Wyoming's coal resources for clean, reliable power generation.

Gasification of High-Ash Chinese Coals Utilizing KBR's Oxygen-Blown TRIG Technology

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Coal Monetization, USA

The KBR transport reactor integrated gasification (TRIG) gasifier has undergone significant development at both the Soil Conservation Service (SCS) Power Systems Development Facility (PSDF) and at the University of North Dakota & Energy Environmental Research Center (UNDEERC). This technology has been demonstrated over 12,500 hours at the PSDF and an additional 3900 hours of gasification testing with over 1200 hours in oxygen-blown mode at the EERC. The TRIG gasification

process is a dry-feed, nonslagging circulating fluidized-bed gasifier, which operates at lower temperatures than other commercially available coal gasifiers. The gasifier has operated successfully on a wide range of fuels, including subbituminous, bituminous, and lignite coals as well as biomass fuel. While capable of processing this wide range of fuels, the transport gasifier is ideally suited to process low-rank coals, which account for roughly half of the proven worldwide coal reserves. Because of the high volatility of low-rank coals, high carbon conversions are achieved with the gasification process without the operational and maintenance issues arising from higher-temperature operation. Key features of the TRIG include 1) simple, well-established design based on technology in use for 70 years which does not require expansion joints; 2) equally effective gasification in either air- or oxygen-blown modes of operation, making it suitable for power generation or production of liquid fuels and chemicals; 3) high reliability, nonslagging design, which allows a 10- to 20-year refractory life; 4) operation without burners, enhancing reliability and minimizing maintenance requirements; 5) use of coarse, dry coal feed, which requires fewer, lower power pulverizers and less drying than other dry feed gasifiers; 6) excellent heat and mass transfer due to a high solids mass flux, with a solids circulation rate much greater than the coal feed rate; and 7) high feedstock throughput per unit cross-sectional area, resulting in a lower capital cost for the gasifier train.

The excellent performance of the TRIG has resulted in the ongoing construction of two commercial projects utilizing air-blown TRIG technology, including a 120-MW integrated gasification combined-cycle (IGCC) system at the Dongguan Tianming Electric Power Company Ltd. (Dongguan TMPEP) in Guangdong Province, Peoples Republic of China, which is expected to begin operation in 2011 along with the 582-MW Kemper County project utilizing Mississippi lignite expected to begin operation in 2014. The TRIG technology has also been receiving considerable interest as coal gasification technology for high-ash feedstocks since the technology does not have the high energy penalty associated with slagging entrained-flow gasifiers and does not have the organics production associated with the dry-bottom Lurgi gasifiers. Successful demonstration of the continuous ash removal systems at the PSDF has also eliminated the operating concerns associated with removing the large quantities of ash from the gasifier train. This paper will discuss the operating results from oxygen-blown testing on three different high-ash, high-rank Chinese coals. Approximately 280 hours of coal feed with the majority of the testing being completed in oxygen-blown mode was successfully completed. The swelling properties of some of the fuels tested were successfully handled without agglomeration problems. Preliminary data tested that corrected syngas heating values were good while obtaining acceptable carbon conversion, although carbon conversion was lower than those experienced with more reactive low-rank coals.

SESSION 21
Coal-Derived Products: General – 4

Robust Nanostructured Noble Metal/ Ceria/Lanthana Catalysts for Water-Gas-Shift

Shuang Liang, Götz Vesper, University of Pittsburgh/DOE/NETL, USA

Noble metal nanoparticles dispersed on oxide supports are widely used as catalysts in fuel processing, chemicals production, and environmental protection. Particularly noble metal/ceria catalyst systems have found much attention due to their excellent activity in partial oxidation and water-gas shift. However, the noble metal nanoparticles suffer from insufficient temperature stability and sensitivity to poisoning in the presence of S-contamination in the reactant feed. Both sintering due to high temperatures as well as poisoning by S-contaminants cause the loss of active surface area and result in irreversible deactivation.

Here, we are reporting on the synthesis, characterization, and testing of robust nanostructured noble metal Au/ceria/lanthana catalysts in Water-Gas Shift (WGS) with S-contaminated syngas feeds. The metal nanoparticles are deposited on nanostructured CeO₂ supports through deposition-precipitation or impregnation. Subsequently, La₂O₃ or La-CeO_x is deposited on the supported catalysts. La₂O₃ has been shown to be an efficient regenerative S-capturing material in the temperature range of interest in WGS. The protective surface modification enhanced thermal stability of the catalyst and enables the catalyst combine simultaneous sulfur capturing with WGS catalysis in a synergistic way.

The catalyst were characterized (TEM, XRD, BET, and TPO/TPR), and tested in cyclic TGA and fixed-bed reactor experiments. WGS activity test in repeated temperature ramps shows greatly improved stability of the active nanoparticle through the surface decoration. First results in repeated sulfidation-regeneration cycles are equally promising, showing fast sulfidation kinetics, large S-capturing capacity, and stable regeneration. Synthesis, characterization, and catalytic activity test will be discussed in detail in the presentation.

High Performance Sour Water Gas Shift Catalyst
Girish Srinivas, Steven Gebhard, Will Spalding, Mike Looker, TDA Research, Inc., USA

Co-feeding biomass with coal in a gasification-based synthetic fuels plant has the potential to reduce carbon dioxide emissions by 50% or more. Unfortunately, the catalysts currently used to convert the syngas from the coal-biomass gasifier are poisoned by compounds that originate in the biomass and coal. Thus, the development of poison-resistant catalysts will advance coal-biomass-to-liquids (CBTL) technology or carbon free integrated gasification combined cycle.

The water gas shift (WGS) reaction that converts the CO in syngas to hydrogen is an important step in all synthetic fuels processes. Hydrogen sulfide (from coal or heavy hydrocarbons) poisons conventional WGS catalysts, and sulfur tolerant WGS catalysts are widely used. Unfortunately, they must be run at higher temperatures than conventional WGS catalysts, and consequently convert less CO to hydrogen (because of equilibrium limitations).

Sulfur tolerant water gas shift catalysts are not only useful for converting coal and biomass to liquid fuels, but are routinely used in gasification or partial oxidation processes that run on coal, coke, bitumen and other heavy hydrocarbon feedstocks. Therefore in addition to synfuels production, our catalyst will also find applications in petroleum refineries, methanol and ammonia plants, and stationary power production.

TDA Research, Inc. (TDA) has developed a new sour WGS catalyst that is as active as conventional low temperature water-gas-shift catalysts and that is not poisoned by sulfur and other contaminants present in syngas produced during the gasification of coal and biomass. Our catalyst overcomes some of the issues of the equilibrium limitations by operating at lower temperatures, where equilibrium favors higher CO conversions. Our catalyst converts more CO to hydrogen, improves the energy efficiency and economics of CBTL, hydrogen, and IGCC plants, and can be used as a drop-in replacement for existing catalysts.

We have tested our catalyst at various H₂O/CO ratios, space velocities, and temperatures. We have also tested our catalyst after deliberately poisoning it with contaminants and have demonstrated that our catalyst is stable under these conditions. Results of these tests will be presented.

Glutaraldehyde Crosslinked Humic Acid and Use for the Adsorption of 4-Tert Butyl Phenol

Hacer Dogan, Tulay Inan, Murat Koral, TUBITAK Marmara Research Center; Selahattin Anaç, Zeki Olgun, TKI, TURKEY

Humic acid produced by TKI (Turkish Coal Enterprises) was crosslinked by glutaraldehyde to make it insoluble in the alkali media. Crosslinking conditions such as time, temperature and concentration were optimized and the products were analysed by the Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analyser (TGA) and scanning electron microscopy (SEM). The humic acid based adsorbent was used for the removal of 4-tert butylphenol, known as phenolic endocrine disrupting compounds that have potential to alter the normal structure or functions of the endocrine system in wildlife and humans. The study showed that crosslinked humic acid could be used as an effective sorbent for the removal of 4-tert butylphenol. The study showed that the adsorption capacity of crosslinked humic acid for 4-tert butylphenol was about 100% .

SESSION 22
Carbon Management: CCS and GHG Abatement – 1

Carbon Capture and Storage Through the Integration of a Chemically and Biologically Catalyzed Mineral Weathering Process with Coal Fired Power Production

Edward J. Swanson, Tushar Patel, Scott Banta, Ah-Hyung Alissa Park, Columbia University; Patrick V. Brady, Sandia National Labs, USA

Accelerated weathering of minerals is an environmentally benign carbon mitigation strategy, and the only approach that produces a thermodynamically and kinetically stable form of carbon. Here, we present a holistic approach to accelerated weathering, integrating it with a coal-fired power plant to create a complete carbon capture and permanent storage process. Previously, accelerated weathering research focused on cost reductions by increasing the reaction rates of individual unit operations, such as mineral dissolution. This approach often leads to brute force attempts to increase driving force or temperature, while missing opportunities for increased efficiency through process integration and catalytic reaction rate increases. In the process presented here, ex-situ multi-step mineral weathering is merged with a power plant, effectively avoiding costs normally associated with capture, purification and transport of carbon dioxide. In addition, chemical catalysis is used to reduce mineral passivation, yielding increased mineral reaction rates and greater utilization of raw materials. A whole-cell biocatalyst is also developed to increase the hydration rate of carbon dioxide, providing an inexpensive and easily recycled catalyst particle that increases the efficiency of carbon dioxide capture. The integration of these innovations

constitutes a novel process for capturing and permanently sequestering carbon dioxide produced during power generation from fossil carbon sources.

Ventilation Air Methane Abatement Projects at CONSOL Energy

Deborah Kosmack, Richard A. Winschel, William P. Fertall, Ryan Blackwell,
CONSOL Energy Inc.; Santosh Lakhan, Verdeo, USA; Jerry Gureghian,
Green Holdings Corporation, UNITED KINGDOM

CONSOL Energy Inc. is participating in the development of two ventilation air methane (VAM) emission abatement projects on their active underground coal mines in southwestern Pennsylvania and the northern panhandle of West Virginia. CONSOL is partnered with Green Holdings Enlow, Inc., for the project in Pennsylvania and with Verdeo McElroy, LLC. (a wholly owned subsidiary of Sindicatum Carbon Capital) for the project in West Virginia. Coal mining, and particularly coal mine ventilation air, is a major source of anthropogenic methane emissions, an important greenhouse gas that is 21 times more potent than carbon dioxide (CO₂). Globally, VAM emissions from U.S. coal mines amount to approximately 300 million tCO₂e (metric tonnes of CO₂ equivalent) each year. Oxidation of methane to carbon dioxide and water reduces its global warming potential by about 87%. The VAM abatement equipment to be installed at the mines will capture and destroy methane released during the mining process that would otherwise be released to the atmosphere through the mine's ventilation system. The combined projects are designed to reduce CONSOL's VAM emissions by the equivalent of 524,000 metric tons of carbon dioxide (tCO₂e) per year. It is expected that both projects will be operational in 2012. Green Holdings Enlow, Inc., and Verdeo McElroy, LLC. will each supply capital, and they will design, engineer, construct, and operate the respective unit, and be responsible for selling the emissions reduction credits. CONSOL will provide the ventilation air fan, the site, and technical support. The progress of each project is discussed herein.

SESSION 23

Combustion: Combustion Studies – 1

Circulating Fluidized Bed Combustion as a Near-Term CO₂ Mitigation Strategy

Eric Grol, DOE/NETL, USA

With the defeat of the CO₂ cap-and-trade regulatory framework in the 111th congress, near-term mitigation strategies for fossil power generation will likely focus on efficiency improvements. Any proposed new unit construction will need to demonstrate competitive heat rates, and particular attention to low emissions of criteria pollutants to adhere to further tightening of air quality standards by EPA. A suite of new air, water, and combustion residual regulations by EPA may potentially force the retirement of a large portion of existing coal units. To ensure an adequate capacity to meet the demand for power, construction of new plants will be required to make up for units that have been retired. Although not a new technology, circulating fluidized bed (CFB) coal-combustion may be the key to meeting this demand. Ultrasupercritical-steam CFB units have demonstrated low heat rates, and the ability to meet stringent air quality standards. In addition, CFB units are fuel-flexible and have the capability to burn carbon-neutral fuels such as biomass (in addition to other opportunity fuels), which reduces the CO₂ footprint of this coal process even further. Judicious design considerations can also allow for eased integration of carbon capture and sequestration (CCS) technology at a future date, making a capture-ready CFB.

Sensitivity Analysis of Models for Particle Air Flames

Scott Rockwell, Ali S. Rangwala, Worcester Polytechnic Institute, USA

The objective of this study is to review the development of theories for computing the characteristics of laminar premixed particle-air flames. Unlike gaseous flames, where conduction, species diffusion, and chemical reaction are important processes, particle-laden flames such as coal-air systems involve additional processes such as devolatilization, particulate radiation, and conduction between gaseous and particulate phases. Development of four theories by Cassel et al. [1], Seshadri et al. [2], Goroshin et al. [3] and Bidabadi and Rahbari [4] are presented. A sensitivity analysis was performed and a discussion on the validity of models for use with coal is presented based on the controlling parameters of each model.

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Effect of Swirl on Unburned Carbon and NO_x Emission of Blending Coal Combustion in a Drop Tube Furnace

Byoung-Hwa Lee, Ho-Lim, Da-Yeon Yu, Ju-Hun Song, Young-June Chang,
Chung-Hwan Jeon, Pusan National University, KOREA

This paper presents that the dependence of unburned carbon and NO_x emission on swirl with blending ratio of sub-bituminous coal in Drop Tube Furnace (DTF). The experiments were performed with blending of sub-bituminous in bituminous coal (single coals and approximately 25%/75%, 50%/50% and 75%/25% blends) at different swirl vane angle (20, 40, 60, 80 deg.) under the condition of 1.3 excess air ratio.

The results show that the unburned carbon decreases as the blending ratio of sub-bituminous coal increase in bunker blending method that two coals is fed into the furnace simultaneously. However, the worst blending condition is found at the 75% of blending ratio, which implies that higher oxygen deficient environment in initial burning region with blending ratio of sub-bituminous coal lead to inefficient combustion of the bituminous coal. The NO_x emission increases as blending ratio of sub-bituminous coal increase due to fuel N containing the coal.

In order to improve the efficiency of unburned carbon and NO_x emission in blending combustion, the swirl force was controlled with variation of blending ratio and coal types. This paper propose that the optimal swirl force in terms of blending ratio and coal types can be reduced unburned carbon and NO_x emission in blending combustion. Furthermore, this paper reveals that the understanding of mechanism on swirl effect in blending combustion has been more clearly clarified.

Experimental Studies of Spontaneous Combustion Propensity of Coal

X.Y. Wang, Y. Luo, West Virginia University, USA

Many factors can affect the spontaneous combustion process of coal as it is mined, stored and transported. These factors include the self-heating potential of the coal, coal rank, geologic and mining conditions, mining practices, ventilation, etc. Among these factors, the self-heating potential is most important. However, spontaneous combustion events in underground coal mines often occur in gob or sealed areas and may not be easily detectable. In storage and shipment conditions, spontaneous combustion normally started under the surface of the coal storage pile and may not be detected initially. Therefore, a better understanding about the propensity of the spontaneous combustion of coal could greatly benefit the planning of these coal mining and handling operations.

Three methods to assess the propensity for coal's spontaneous combustion, USBM, R70 and TGA, will be discussed. The USBM and R70 heating rate methods were developed in US and Australia, respectively. However, the empirical formulae developed by the USBM researchers, though simple, seem to predict the propensity of a coal sample in a large range, creating possible uncertainty. The experiments required by R70 method is time consuming and tedious. The thermal gravimetric analysis (TGA) is a relatively new quantitative method in studying coal's self-heating potential with a sound theoretical basis. In a relatively short period of experiment on a small coal sample, the oxidation process of coal can be simulated in a precisely controlled environment. The measured temperature and weight can be used to calculate the kinetics and activation energy of the coal which in turn is a good indicator for the propensity of spontaneous heating.

Coal samples from a number of US coal fields have been collected and tested using R70 and TGA methods. Comparison of the test results is presented and the relationships among the three methods are discussed.

1-D Dynamic Modeling for Moving Bed Reducer in Chemical Looping Process

Qiang Zhou, Liang Zeng, Hui Yang, Zhao Yu, Dawei Wang, Fanxing Li,
Liang-Shih Fan, The Ohio State University, USA

Chemical looping combustion (CLC) and chemical looping gasification (CLG) are effective strategies for electricity generation and hydrogen production from coal derived syngas with in-situ CO₂ capture. The reducer or the fuel reactor in the chemical looping process converts syngas with the oxygen carrier particles. Accordingly, it is important to study the reaction behavior and reducer performance under given reactor geometries and operating conditions. In this work, the reaction kinetics for iron oxide based oxygen carrier particles are characterized by a three-interface unreacted shrinking core model. An one-dimensional (1-D) flow model is developed to simulate the countercurrent gas-solid flow pattern within a moving bed reducer. The flow model governs the mass balance between gas phase and solid phase, and includes a time derivative term, which can help to obtain the whole evolution process of the reaction in the moving bed reducer. The new flow model together with a three-interface shrinking core model is executed by using Matlab codes. It is noted that the 1-D moving bed reducer model converges much faster compared with the 2-D CFD model, which can accordingly serve as a powerful tool for further 2-D reducer modeling. The 1-D moving bed code has been validated through comparing the results with those of previous experiments from iron ore reduction industry. Using the mathematical model, important reducer performance data such as the gases and solids conversions and gas and solid compositions can be obtained. The 1-D reducer model can tell how long it

will take for a specific moving bed to reach its steady state. We can also learn the information of the minimum bed height required to completely convert fuel gas.

SESSION 24 Coal Science: Coal Geology

Geochemistry of Mineral and Carbon Nanotube Sublimate Assemblages in Coal Fire Soot, Ruth Mullins Fire, Perry County, Kentucky

James C. Hower, Shelley G. Hopps, Kevin R. Henke, University of Kentucky CAER; Jennifer M.K. O'Keefe, Morehead State University; Christopher S. Romanek, University of Kentucky, USA; Luis F. O. Silva, Marcos L. S. Oliveira, Vivian Philippi, Catarinense Institute of Environmental Research and Human Development – IPADHC, BRAZIL; Carmen Serra, Universidad de Vigo, SPAIN; Shifeng Dai, Weifeng Xue, Wenmei Chen, China University of Mining & Technology, CHINA

Coal fires in eastern Kentucky generally occur in abandoned mines. In the case of the Ruth Mullins fire, Perry County, the source of samples in this study, the fire developed in the remnants of a succession of underground, contour surface, and auger mines active intermittently from the 1930's to late 1950's. Based on anecdotal evidence from conversations with local residents, the fire has been burning since about 1960. Investigations of minerals and sooty carbons at the fire reveal a complex assemblage of sublimated mineral and carbon forms, the latter including nanotube-bearing soots and PAH-rich tars.

While the mineralogy is dominated by salammoniac, HR-TEM/EDS, FE-SEM, TOF-SIMS, among other microbeam tools, reveals a complex assemblage of nanometer-scale As-, Pb-, and Se-bearing minerals. Ultrafine minerals include pyrite, jarosite, hematite, pickeringite, barite, and gypsum. Sooty, nanotube-bearing carbons have over 5 ppm Hg. Unlike superficially similar soot from a coal-fired stoker power plant, the coal fire soot does not contain any indication of fullerenes in the m/z 650 to 970 amu range.

Effect of Weathering of Coal and Organic Dusts on their Spontaneous Ignition

K. A. Joshi, A. S. Rangwala, Fire Protection Engineering, Worcester Polytechnic Institute, USA; V. Raghavan, Indian Institute of Technology Madras, INDIA

Weathering of coal and other cellulosic dusts occur due to the process of wetting and subsequent drying, or by subjecting them to a temperature higher than the ambient temperature for prolonged time periods. The first type of weathering occurs in airtight storage. The second type of weathering occurs when a dust processing unit stores and maintains the dust deposit at an elevated temperature. As a result of weathering, the physical and thermal properties of the dust may change. Therefore, the weathered dust is expected to ignite at a different temperature, when compared to that of a fresh sample. In this study, a standard test method (ASTM E 2021) is used to determine the safe surface temperature, which would avoid self-heating of a weathered combustible dust deposit. Weathering of two types coal dust samples (a) wheat flour, (b) Pittsburgh seam coal and (c) powder river basin coal are carried out by two techniques; namely, (a) controlled wetting and drying of coal dust and (b) subjecting the coal dust to a uniform temperature, 70 °C below the minimum surface ignition temperature obtained using a fresh sample, until no further change in temperature occurred at any height in the dust layer. The implications of the observed results on industrial safety measures related to combustible dust layers are discussed.

Fe-Nanominerals in Sediments from Coal Mine Drainage

Frans Waanders, North West University, SOUTH AFRICA; Luis F. O. Silva, Marcos L. S. Oliveira, Kátia da Boit, Catarinense Institut of Environmental Research and Human Development – IPADHC, BRAZIL

Numerous questions exist on nanominerals formed in coal mine drainage sites and by reactions at interfaces. This paper uses data from detailed mineralogical and geochemical studies conducted at Brazilian coal mining zone where Fe oxyhydroxide nanoparticles appear to go through structural transformations dependent on their size and formation conditions. In addition, the mineralogy and chemistry of the Fe precipitates (e.g. jarosite, goethite, hematite), present in the CMD-generating mine sites, have also been detailed studied because hematite, which is a potential source of Cr, is relatively stable in extremely low-pH conditions.

Organic Petrology of the Springfield Coal Marine Shale Roof Rock (Turner Mine Shale) in Western Kentucky

Cortland F. Eble, University of Kentucky, USA

The Springfield coal bed occurs near the middle of the Carbondale Formation, and represents one of the most widespread and heavily-mined coal beds in the Western Kentucky Coal Field. Samples of the Springfield coal and overlying roof shale (Turner

Mine Shale) were collected as part of a study to determine the coal bed methane potential of western Kentucky coal beds. Direct gas desorption measurements of five Springfield core samples indicate that it ranges from 110 scf/ton methane (as received basis), in deeply-buried (>1000 ft of cover) areas, to 40 scf/ton in areas with shallow cover, or adjacent to active mining. Desorption measurements of the overlying shale from four locations indicate a range from 30 to 50 scf/ton of methane (as-received basis). Although neither lithology (coal or shale) can be presently considered as an economic gas resource individually, they may collectively represent a potential gas resource in western Kentucky. This study focuses on the organic petrology of the Springfield coal and overlying Turner Mine shale.

Organic petrologic analysis of the shale indicates that liptinite macerals, especially bituminite, are much more common in the Turner Mine shale (avg. 36.1 %, mineral matter free, mmf, basis) compared to the Springfield coal (avg. 6.7 %, mmf). Bituminite in the shale exhibits a wide range of morphology and fluorescence characteristics.

Inertinite contents are also higher in the Turner Mine shale (avg. 29.4 %, mmf), compared to the coal (avg. 11.7 %, mmf). A type of macrinite with a “granular” appearance is very common in the shale.

Vitrinite contents are much lower in the shale (avg. 34.5 %, mmf) than in the coal (avg. 81 %, mmf), with “unstructured” forms (detrovitrinite and gelovitrinite) being more abundant than “structured” forms (telovitrinite).

SESSION 25 Major CCS Demonstration Projects: General – 2

China's CCS Actions, Initiation and Reservation

Huaibin Lu, 3E Information Development & Consultants, USA

China burns near a half of coal in the world, and relies on coal to meet 70 percent of its energy needs. Of the current one billion MW installed power generation capacity in China, 74 percent is coal-fired, and a half of the country's coal supply is fed into those power plants. These impressive numbers would in little doubt deduct a conclusion that coal, particularly coal-fired power generation sits well in the center of China's energy strategy and environment policy on energy saving, alternative fuel development, clean fuel technologies and emission reductions.

In a global wave of developing clean fuel technologies, fighting global warming and pursuing sustainable development, China has been active in applying clean and highly-efficient coal-fired power technologies including USPC, SUPC and IGCC, and is moving positively but cautiously in taking CCS actions. The share of installed USPC and SUPC has now accounted for over 10 percent of the country's total installed power capacity, and is expected to approach 30 percent and 50 percent by 2020 and 2030 respectively according to central government's long-term plans. The first IGCC plant is scheduled into production in Tianjing by 2011.

After an initial learning stage with cooperative projects sponsored by foreign players, major state-run energy companies are setting up a few CCS demonstration programs in China. Several large power plants have built CO₂ capture facilities in Beijing, Shanghai and Chongqing with annual CO₂ fixing up to 10,000 tons each. CNPC has for years conducted successful EOR operations with CO₂ injection in a Northeast oil field. The most recently, Shenhua Group has begun running a full-course CCS demonstration project in its pilot CTL plant in Inner Mongolia, storing CO₂ of 100,000 ton per year into a 3,000 meters deep underground cavern.

Behind the movement in China lie several influencing factors and motives.

- Checking ever-growing energy demand and securing sustainable development have risen into the country's top agenda;
- Severe environment degradation is stirring widespread social concerns of pollution controls;
- As the 2nd largest economy and the top energy consumer and CO₂ emitter, China is confronted with growing international pressures.
- China is to compete for a leading position in developing green technologies in a new round of industrial technological revolution.

Chinese government has made a commitment to cut per GDP energy consumption by 40 to 45 percent (and CO₂ emission reductions as well as a sequence) by 2020. However, investment and measures so far are mostly focused on practical elements such as energy saving, clean coal technologies and renewable energy development. CCS actions are still at initial and middle levels of academic debates and state-run companies' showcases, having not yet entered the mainstream energy strategy and environment policy of the central government.

Potential opportunities of the Chinese CCS market are no doubt among the largest. At the present however, investment is solely made by state-run companies, and no decisive government plans, laws and regulations, financing options, and risk management vehicles have been established. There would be great uncertainties and risks for outsiders without clear guidelines, transparent market mechanism and operating rules.

Future development of CCS programs in China will likely depend on the following factors.

- Will international pressures of global warming continue mounting up along with progress of international negotiations of carbon emission reductions;
- How will the structures of the Chinese economy (export-oriented and heavy industries in particular) and energy supply and consumption in the country evolve in the future;
- Will carbon taxation or similar be introduced into China in a near future;
- How quick will breakthroughs of efficient and cost-effective green technological particularly for CCS be achieved;
- To what extent will the political, legal, industrial and financial systems in China be improved to facilitate investment in CCS.

Fluidized Bed Low Rank Coal Drying: Great River Energy's Coal Creek Station Experience

Charles Bullinger, Great River Energy, USA

Following through on its successful proposal to the U.S. Department of Energy's Round 1 Clean Coal Initiative Program project # DE-FC26-04NT41763, Great River Energy has now installed and commissioned a fluid bed-based fuel drying process on both the lignite-fired 600 MW units at their Coal Creek Station. The process utilizes station waste energy to dry 100% of their fuel. Called DryFining™, it also results in removal of sulfur- and mercury-bearing ash components through density beneficiation. The complete system was put into service 4Q2009. It has been in reliable, continuous service since then.

Per DOE CCIP requirements, the DryFining process has been both pre-and post-installation performance tested by an independent contractor. Following the unit Outage in the Spring of 2011, a final performance test will be completed. Further, parallel analysis of longer term operations and maintenance performance and cost data will also be coming available. Great River Energy and WorleyParsons are actively pursuing marketing DryFining since it's benefits could be realized on nearly half of the global reserves.

This paper provides an historical overview of the project, outlines the formal performance results, examines the influence of fuel drying on O&M costs, and discusses some of the lessons learned.

Overview of the Kemper County and TMEP IGCC Projects Using Transport Integrated Gasification (TRIG™)

Randall E. Rush, Tim Pinkston, Matt Nelson, Guohai Liu, Southern Company, USA

Mississippi Power Company is building a 2 x 1 Integrated Gasification Combined Cycle (IGCC) facility in Kemper County Mississippi. The plant which is based on Transport Integrated Gasification (TRIG™) technology—developed by Southern Company, KBR, and the U. S. Department of Energy (DOE)—will use local Mississippi lignite and produce 582 MW at peak and 524 MW on syngas. Ammonia, sulfuric acid, and carbon dioxide will also be produced. Over 65% of the carbon dioxide will be captured and used for enhanced oil recovery (EOR), making the Kemper facility's carbon emissions comparable to a natural gas-fired combined cycle power plant. The Kemper County project is currently in the detailed engineering and construction phase with all major equipment under order. Detailed design is scheduled to be completed by the third quarter 2012 and the facility Commercial Operation Date (COD) is set for May 2014.

TRIG™ technology is also under construction at a nominal 120 MW facility currently being installed as a retrofit to existing gas turbines in DongGuan City, Guangdong Province of China for Tian Ming Electric Power (TMEP) Company, Ltd. A single TRIG™ unit will provide syngas from Indonesian lignite for two existing General Electric 6B gas turbines (supplied by Nanjing Turbine and Electric Machinery Group Ltd.). Commercial operation is expected in 2012.

This paper will outline the TRIG™ technology and highlight the status of these two projects.

RTI Warm Syngas Clean-up and Carbon Capture Sequestration Project

Ben Gardner, Raghubir Gupta, Brian Turk, RTI International, USA

Currently, coal is used to generate 48.5% of the electricity used within the United States. Furthermore, coal, because of existing infrastructure, abundant resources, and commercially available technologies, will likely remain the predominant fuel for electric power generation for the foreseeable future. Although coal has a legacy of being a "dirty" fuel, technology advances, particularly integrated gasification combined cycle (IGCC) plants, have been shown to provide near zero emissions from coal-fired power plants. However, commercial deployment of new more efficient and cleaner coal-based IGCC plants has been very slow due to concerns related to high capital costs, low availability, and high technology risks.

RTI has developed a warm syngas desulfurization process that has been demonstrated at both lab and pilot scale. Results from the lab and pilot tests have shown that RTI's technology can improve both efficiency and cost (capital and operating) on IGCC plants. Therefore, a larger scale demonstration of the process is required to mitigate the technical and scale up risk associated with commercial deployment. RTI with the funding from the U.S. Department of Energy is building a 50 MW demonstration of this warm syngas clean-up technology platform with the goal of being ready for

commercial deployment by 2015. The project scope also includes carbon capture and sequestration (CCS). RTI will locate the project at Tampa Electric's IGCC plant at Polk Power Station outside of Tampa, Florida. A slipstream of syngas will be treated in the warm gas desulfurization process. Once treated, the clean syngas will be sent to a series of shift reactors where CO will be shifted to H₂ and CO₂. Next, the CO₂ will be separated from the syngas in a commercially available acid gas removal system. The CO₂ rich stream will be compressed, dried, and sequestered, while the H₂ rich stream will be returned to Tampa's existing combustion turbine.

The goals of this project are to demonstrate that the warm gas desulfurization technology can remove >99.9% of H₂S and COS from coal derived syngas, operate for 8,000 hours, capture 90% of CO₂, sequester up to 300,000 tons CO₂/year, and monitor the CO₂ activity underground. The results from this project will be used to establish performance criteria for stable commercial operation including reliability, availability, and maintenance (RAM) and provide extensive operating experience including startup/shutdown and operator training. The results from the demonstration project will be utilized to validate the current performance and economic models. This paper will provide details on current project scope, cost, schedule, and anticipated challenges, in particular, permitting, injecting, and monitoring and accounting of CO₂ storage underground at the Polk Power site in Florida.

SESSION 26

Gasification: Coal & Biomass

Reaction Kinetics and Product Distributions from Pyrolysis of Coal and Biomass Mixtures

Nicholas C. Means, URS/DOE/NETL; Nathan T. Weiland, West Virginia University/DOE/NETL; Goetz Vesper, University of Pittsburgh/DOE/NETL; Ronald Breault, Chris Guenther, DOE/NETL, USA

The United States Department of Energy's National Energy Technology Laboratory (NETL) is working to develop technologies that reduce the cost of electricity, while increasing power plant availability and efficiency, and maintaining the highest environmental standards. Coal, an abundant natural resource, can be utilized by thermochemical processes to produce electricity, hydrogen, liquid fuels or other chemicals. Co-gasification of coal and non-food oriented biomass can prolong national fossil energy resources while reducing net greenhouse gas emissions. In order to better understand co-gasification phenomena, both pyrolysis and gasification reactions will be investigated at various feed compositions and reactor conditions. The focus of this study is to evaluate of the complex pyrolysis reaction and to provide fundamental co-pyrolysis and co-gasification kinetic data under transport gasifier conditions for inclusion into NETL's Carbonaceous Chemistry for Computational Modeling (C3M) platform.

An experimental study on isothermal co-pyrolysis of Illinois#6 coal and switchgrass was done in a tubular drop reactor at atmospheric pressure and temperatures ranging from 700-950°C. Co-pyrolysis experiments were performed in an effort to gain an understanding of the effect of coal-biomass co-feed on reaction kinetics and gaseous, liquid and solid product distributions. Coal and biomass were fed to the reactor with varying feed ratios. Primary gaseous products (CO, CO₂, CH₄, H₂ and H₂O) were monitored and analyzed online using quadrupole mass spectrometry. Trace gaseous products were collected as a batch and analyzed using gas chromatography/mass spectrometry. Tar/liquid product analysis was done using gas chromatography/mass spectrometry and residual solid analysis was done with inductively coupled plasma optical emission spectroscopy. Initial results indicate that the addition of biomass to coal during pyrolysis does not cause a significant deviation from the linearly expected product distributions based on the pure species; however, it may influence pyrolysis reaction kinetics due to synergistic coal-biomass interactions.

Enhanced Methane Production by Co-Gasification of Potassium-Rich Biomass and Coal

Mike Bockelie, Kevin Davis, Andrew Fry, Adel Sarofim, Reaction Engineering International; Kevin Whitty, Chris Claxton, University of Utah, USA

Natural gas, which is predominantly methane, is widely used by industry as a chemical feedstock and as a fuel for power generation. The unstable price and uncertain nature of resource development of natural gas creates an incentive to develop a low-cost replacement for the fuel. Coal gasification is one approach to provide the alternative fuel. However, the dominant commercially available coal gasifiers are not designed or operated to provide large amounts of methane. Through funding from a DOE STTR Phase I project, Reaction Engineering International (REI) has investigated enhanced methane production from the co-gasification of potassium-rich biomass and coal. The use of potassium and other alkali metals to catalyze coal gasification is well established. In the presence of alkali metals, the gasifier can operate at lower temperatures and pressures. Providing the potassium in the biomass avoids the need for expensive, proprietary catalysts that increase the cost of the gas produced. In this paper

we provide an overview of small experiments, modeling calculations and a technical market evaluation for a recent investigation of enhanced methane production.

Thermodynamic Modeling of Coal and Biomass Co-Gasification

Aime H. Tchapda, Sarma V. Pisupati, Pennsylvania State University, USA

The world's coal stock is still relatively high compared to oil and gas. It has a relatively low cost and a high energy density. As the cost of oil and natural gas continue to increase, the conversion of coal to liquid and chemicals is projected to become preponderant in the petrochemical industry. Therefore, it is expected to contribute significantly in the future energy needs of the world. However, this projection may not be accurate if adequate methods are not developed to make its utilization cleaner. Thermo chemical conversion of coal results in large emission of undesirable products including carbon dioxide, acid rain precursors such as oxides of sulfur (SO_x) and oxides of nitrogen (NO_x), particulate and trace elements such as mercury (Hg), to name just few. The need to mitigate these negative environmental effects, and to substitute the depleting and highly polluting fossil fuels have led to the development of alternative sources of energy and utilization of low quality, but environmental friendly fuels like biomass and waste. Biomass as gasification feedstock gives a high hydrogen yield. Its high oxygen content also makes it very reactive. However, due to the low energy density and seasonal limitation, dedicated biomass gasification is limited to small scale and localized applications. Co-gasifying coal and biomass can take advantage of the mutual advantages of each fuel. It is therefore, important to understand the thermo chemical conversion behavior of coal and biomass blends.

In this study, thermodynamic equilibrium of coal and biomass co-gasification has been modeled. The effect of blend ratio, temperature and pressure, on the gas composition was studied. Cold gas efficiency and gross calorific value of the product gas have been analyzed. It is found that the concentration of carbon containing compounds in the product reduces as the ratio of biomass in the blend is increased, while that of the hydrogen containing compounds increases. This has a direct effect on the cold gas efficiency and the gross calorific value. In general, the gross calorific value and cold gas efficiency were found to increase as the ratio of biomass in the blend (on an energy basis) increases. The optimum temperatures where the highest cold gas efficiency and gross calorific value occurred is between 1200 and 1400°C. Increasing the pressure reduces the cold gas efficiency and gross calorific values but at higher temperatures (> 1400°C) the effect of pressure is found to be insignificant.

SESSION 27

Coal-Derived Products: General – 5

Development of Thar Coal: Putting the Pieces Together

Farid A. Malik, Munawar Baseer Ahmad, EMR-Consult, PAKISTAN

Thar coal deposit ranks as one of the largest contiguous coal reserves (175 billion tons) in the world. While Pakistan continues to suffer from serious energy shortages, this huge resource remains untapped. Several government entities and public sector organizations have been struggling to exploit this gift of nature. Engro Energy & EMR Consult in the private sector have been leading the efforts to put the Thar Coal Resources Development efforts on the right track.

Sufficient geological data is now available to move ahead for the mining development and downstream applications. The challenge and the opportunity is to develop an economically viable and environmentally friendly methodology on a mega scale. However in order to establish the economics and mine engineering parameters it is deemed essential to start with a smaller development mine to establish the mine ability and economics of the deposit. Once the bulk samples have been mined, the IGCC approach along with FTD, SNG etc approaches based on clean coal technologies and on a co-production concept, can be adopted for maximum utilization of the mined coal. This will provide for the basis of a real bankable feasibility, which is essential to secure project financing. Several deadlines have been set and missed already but the clear need is to have a robust "Master Plan" for Thar Coal Resources development.

An attempt has been made by EMR-Consult to put the developmental pieces together. Starting from scoping studies, and mine development, leading to gasification/liquification/fertilizer process development to production mine and large scale gasification have been covered. One approach is that after mining the coal will be gasified at the mouth of mine and the synthetic natural gas (SNG) be transported through the national underground gas pipeline network for power generation and fertilizer production where needed. A deposit of this size needs a holistic Master Plan which has been developed by EMR-Consult but not implemented yet.

The Technical and Economic Feasibility of Siting Synfuels Plants in Wyoming

Anastasia Gandrik, Richard D. Boardman, Rick Wood, Idaho National Laboratory; David Bell, William Schaffers, Thomas Foulke, University of Wyoming, USA

A comprehensive study has been completed to determine the feasibility of constructing and operating gasification and synfuels plants which convert Wyoming fossil resources (coal and natural gas) into higher value products, including electric power, synthetic transportation fuels, and chemical feedstocks, such as ammonia and methanol. Conceptual plant designs, simulation models, economic models, and well-to-wheel greenhouse gas models were developed in order to address the following topics:

1. Quantification of plant capital and operating expenditures
2. Plant heat integration
3. Quantification of coal, natural gas, electricity, and water requirements
4. Access to raw materials and markets¹
5. Requirements for new infrastructure, such as electrical power lines and product pipelines¹
6. A cost-benefit analysis of using natural gas reforming versus coal gasification for synfuels production
7. Labor resource requirements for plant construction¹ and for permanent operations
8. Options for managing CO₂ emissions, including capture and use in enhanced oil recovery and/or sequestration
9. Options for reducing water requirements, such as recovery of the high moisture content in Wyoming coal and use of air coolers rather than cooling towers
10. Permitting requirements¹
11. Construction and economic impacts on the local communities¹

This paper will summarize the analysis completed for two major synfuels production pathways, methanol to gasoline and Fischer-Tropsch diesel production, using either coal or natural gas as a feedstock.

- 1) Results for these topics will not be covered in this paper, please see INL/MIS-11-22553 for the complete project results summary.

Scale-Up of Hydrogen Transport Membranes for Carbon Capture Applications

John Faull, Doug Jack, Carl Evenson, Richard Mackay, Jason Stotter, Eltron Research and Development Inc, USA

Eltron Research & Development Inc. will present an update on the scale-up of Eltron's hydrogen separation and carbon capture membrane technology. In partnership with the Department of Energy (DOE), Eltron has developed a process technology that economically separates high purity hydrogen from a mixed gas feed stream. This technology will enable carbon capture in coal gasification facilities for power and chemicals production; other applications are also being explored.

Eltron is currently accelerating technology development through three scale-up steps. The first step is a reactor designed to separate up to 12 lbs/day of hydrogen from shifted coal-derived syngas, which has been installed at Eastman Chemical Co.'s site in Kingsport, TN. Results will be presented on operation and performance of this membrane system. The second step is a 20x larger process development unit that will also be installed and operated at Eastman's site. Progress on design of that system will be presented. Finally, Eltron was awarded ARRA funding by DOE to further scale-up this technology to the pre-commercial scale. This work will culminate in the operation of a nominally 4-10 T/day membrane reactor. Site selection and Pre-FEED engineering tasks will be discussed.

Modeling Fine Particle Pollution From Aircraft Using JP8, Fischer-Tropsch and Blend Fuels

Shantanu Jathar, Marissa Miracolo, Ngoc Nguyen, Albert Presto, Greg Drozd, Allen Robinson, Center for Atmospheric Particle Studies (CAPS), Carnegie Mellon University, USA

Aircraft emissions of fine PM during ground operations can contribute significantly to local/regional air pollution. Recently, Miracolo and coworkers (Miracolo et al., 2011, Miracolo et al., in prep) found that aircraft engine emissions, when exposed to sunlight, form substantial secondary organic aerosol (SOA) mass compared to the primary PM mass, regardless of the fuel used (JP8, Fischer-Tropsch (FT), 50/50 JP8-FT blend). When we run an updated model that accounts for the traditional SOA (T-SOA) formation from volatile organic compounds (VOCs), the model is able to predict a quarter to half of the SOA measured in experiments conducted at different engine loads and fuels. Recent evidence suggests that the rest of the mass, termed non-traditional SOA (NT-SOA) could originate from the gas-phase oxidation of semi-volatile and intermediate volatility organic compounds (SVOCs and IVOCs). While SVOCs stem from the evaporation of primary organic aerosol (POA), IVOCs represent a class of compounds that are not routinely measured and therefore not included in models. In this work, we propose to build a model that accurately represents the entire SOA production from aircraft emissions with an effort to holistically evaluate the secondary PM formation resulting from the use of JP8, FT and 50/50 JP8-FT blend fuels. For NT-SOA, we propose a new mechanism to represent its formation from aircraft SVOC and IVOC emissions. We use the technique developed by Nguyen et al.

(in prep) to measure and distribute SVOC and IVOC emissions in volatility space. The SVOCs (considered together) and IVOCs (considered together) are treated as surrogate species and the methodology used to fit SOA formation from VOCs is applied to determine SOA mass yields for the SVOC and IVOC surrogates. A single set of volatility basis set (VBS) yields is able to explain the observed NT-SOA formation across engine loads for each fuel type. This implies that the potential of SVOCs and IVOCs in aircraft emissions to form SOA does not change with engine load, which significantly simplifies its representation in models. When simulated in a plume model, the treatment of SOA increases the carbonaceous PM mass loading from aircraft engines using JP8 by 70%. We intend to run the same plume model to examine the evolution of emissions from aircraft engines running FT and 50/50 JP8-FT blend fuels.

SESSION 28

Carbon Management: SECARB-ED CCS Training Session – 1

Why Carbon Sequestration?

Steven M. Carpenter, Advanced Resources International, USA

As power producers fight the battle between demand vs. carbon reduction, one of the essential tools will be capture and storage (e.g. sequestration) of carbon. Understanding Green House Gas (GHG) emissions and strategies will afford open dialogue and better understanding of the implications of carbon management. Presently there are seven DOE funded regional partnerships pursuing technical and marketable applications for carbon capture and storage. These partnerships have revealed application successes and constructability realities that must be addressed in order for this technology to become marketable and more importantly, used by industry. An overview of the several regions progress will be presented and some specific details of the SECARB projects will be shared. Implementation issues, economics and potential roadblocks will be discussed and the audience will be engaged to consider possible options to overcome these possible setbacks.

Carbon Capture and Storage (CCS) - Examples From the Field

Timothy R Carr, West Virginia University, USA

The goal of geologic storage (GS) carbon dioxide (CO₂) is to reduce the amount of greenhouse gas (GHG) emissions in the atmosphere by ensuring safe, secure, and verified long-term storage in geologic formations. This part of the SECARB-ED short course provides an introduction and overview of best practices that have been documented during NETL-funded demonstration projects for small-scale and commercial-scale carbon capture and storage (CCS) projects. NETL is actively developing and demonstrating practical, safe, and effective CCS projects where CO₂ is captured at a source, transported to a suitable location, and injected into deep geologic formations for long-term storage. The goal is to demonstrate that CO₂ can be successfully and securely stored over extended periods of time in a manner that is compliant with the best engineering and geological practices; Federal, State, and local regulations; and the best interests of local and regional stakeholders. This will directly link the national interest in reducing greenhouse gases with regional and local economic, environmental, and social interests. Design and implementation of CCS projects span multiple years and involve multiple activities including:

- Site Selection and Characterization
- Operational Simulation and Risk Assessment
- Well Construction, Operations, and Closure
- Monitoring Verification and Accounting
- Public Outreach and Education
- Post-Closure Risks and Liability

Successful implementation of GS projects requires developers to compare critical parameters among candidate sites including: storage capacity; impact on health, environmental safety and economics; local regulatory constraints; monitoring efficacy; and potential ancillary benefits (e.g., enhanced hydrocarbon production). Best practices applied to CCS implementation can provide stakeholders (operators, project developers, general public, and regulators) with information to better understand GS associated with a CCS project including: operations, economic costs, potential risks, benefits, consequences and the long-term fate of long-term CO₂ storage.

As of March 2011 the US Department of Energy's National Energy Technology Laboratory (NETL) has published four Best Practice Manuals (BPMs) covering: (1) "Monitoring, Verification, and Accounting of CO₂ Stored in Deep Geologic Formations," (2) "Public Outreach and Education for Carbon Storage Projects," (3) "Site Screening, Selection, and Characterization for Storage of CO₂ in Deep Geologic Formations", and "Risk Analysis and Simulation for Geologic Storage of CO₂". These manuals present important information on demonstration project results and recommended practices that can be used by regulatory organizations, project developers, and national and State policymakers to ensure the safety and efficacy of carbon storage projects.

Fundamentals of Carbon Sequestration in Coal and Shale

Jack Pashin, Geological Survey of Alabama, USA

Coal and shale are continuous-type, unconventional reservoirs that currently account for much of the natural gas produced in the United States. These reservoirs also have potential to store vast quantities of anthropogenic CO₂, and injection of CO₂ shows promise as a technique for enhancing natural gas recovery. The reservoir properties of coal and shale differ substantially from those of conventional sandstone and carbonate strata, and so a spectrum of laboratory techniques have been developed specifically to characterize coal and shale. These techniques include proximate analysis, ultimate analysis, rock-eval pyrolysis, tight-rock analysis, adsorption isotherm analysis, and desorption testing. Coal and shale are organic-rich rocks characterized by a microporous framework and natural fracture networks. Gas is stored in free and adsorbed states within the microporous framework, whereas natural and induced fracture networks facilitate commercial flow rates. Indeed, flow in microporosity can be dominated by diffusion, whereas that in open fractures is dominated by Darcian flow.

A thorough understanding of the geology of coal and shale is essential to evaluating reservoir properties and the potential for natural gas production and carbon storage. Many reservoir properties, such as thickness, continuity, and composition, are determined in the original depositional environment. Tectonic deformation and fracturing affect bed geometry and continuity and the ability of coal and shale to store and transmit fluid. Burial history and basin hydrology exert a strong influence on the geochemistry, pressure regime, and geothermics of unconventional reservoirs. Indeed, reservoir petrology and gas storage mechanisms should be investigated to determine the storage capacity and mobility of reservoir fluids. For example, adsorbed gas tends to have greatest mobility in shallow, cool formations, whereas free gas maintains near-constant mobility across a spectrum of reservoir conditions.

SESSION 29

Combustion: Chemical Looping – 1

Thermogravimetric Analysis of CuO Chemical Looping by Oxygen Uncoupling (CLOU): Dependence on Sample Size and Oxygen Content

Blake R. Wilde, Edward M. Eyring, Gabor Konya,
The University of Utah, USA

Thermogravimetric analysis (TGA) has been proven to be a useful method for the kinetic analysis of chemical looping combustion. This study focuses on the oxidation of copper(I) oxide and the release of oxygen from copper(II) oxide. The kinetic parameters of these two reactions were found to vary by using different TGA instruments. It is shown that the rate of reaction is dependent upon sample size, exposed surface area, and the partial pressure of oxygen. Utilizing known variables, calculations bring the observed reaction rates on different TGAs into agreement.

Application of Natural Ores as Oxygen Carriers in Chemical-Looping Combustion

Hanjing Tian, Tom Simonyi, Ranjani Siriwardane, URS/DOE/NETL, USA

Chemical looping combustion (CLC) is a combustion technology that utilizes oxygen from oxygen carriers such as metal oxides instead of air to combust fuels. The significant advantage of a CLC system is that a concentrated CO₂ stream can be obtained after water condensation without requiring any energy for separation of CO₂. In addition, NO_x production is also greatly reduced. Oxygen carrier development is critical for applicable CLC process. Synthetic materials containing Fe, Cu, Ni and Mn oxides with inert supports have been tested extensively by various research in the past. However, the application of natural minerals as oxygen carriers has not been fully investigated. The main advantages of using natural minerals are the lower cost and much abundance.

The objective of this paper is to investigate the performance of natural ores based on Fe and Cu oxides oxygen carriers for coal and natural gas CLC. The materials were tested in thermo-gravimetric analyzer and a laboratory fixed bed reactors with coal or natural gas as fuels. Most natural minerals showed lower combustion capacity than synthetic oxygen carriers due to low-concentration active species. The reactivity of CuO-based minerals was better than that of FeOx based minerals. CuO ores can be directly used as oxygen carrier for chemical looping with temperature below 800 °C. Steam must be added for FeOx based ores in CLC to obtain acceptable reaction performance. During methane CLC, carbon deposition was observed during reduction of FeOx based minerals.

Instrumentation for Solids Transport Level and Mass Flow Rate

Joe Quinn, Majid Chaudhry, Alstom Power Inc., USA

Regardless of the specifics of the process, all solids transport based coal power generation plants rely on accurate knowledge of material inventory and transport rates in order to control and optimize energy production and combustion reaction rates. The higher the process operating temperature and the more complex the reaction chemistry the greater the need for knowing material inventory levels and transport rates at critical locations within the process flow. This paper reports on the work performed by Alstom Power in 2009-10 to investigate and evaluate new advanced sensing approaches to process measurements of solids level and flow.

This paper covers the performance features of five level sensing technologies evaluated. The level sensors considered included both discrete and continuous level detection methods.

In order to develop a quantitative assessment of the performance potential for each level sensor technology evaluated a fifteen-point evaluation criterion was developed. This evaluation criterion incorporated performance aspects specific to the harsh operating environment, high solids temperature > 2000°F and long operational intervals expected of instruments operating in the power generation sector. High composite scores are indicative of strengths and weaknesses of each sensor technology and predict the likelihood of becoming a successful instrument for commercial scale process applications.

Solids Mass flow rate in a two phase (gas/solid) regime has been and remains an area of intense investigation. The measurement of solids mass flow rate in a riser or transport piping is the simultaneous determination of the solids flux (kg/cm² sec) at each point in the pipe cross-section. This can practically be achieved by simultaneously determining solids velocity and solid density. In the study, priority was given to near term technologies which had the potential to become low to moderate cost commercial instruments.

Since commercial solids mass flow instruments exist in the process industry, the evaluation focused on the evaluation of two current product offerings and an assessment of the amount of adaptation these instruments would require to become a useful mass flow measurement in the demanding application of high temperature solids transport. A single new technology for solids mass flow measurement utilizing capacitive tomography was also evaluated in terms of its trajectory to commercial application in an industrial process setting.

Bench-Scale Testing of Char Conversion Using a Countercurrent Moving Bed Reducer in the Coal Direct Chemical Looping Process

Samuel Bayham, Liang Zeng, Siwei Luo, Ray Kim, Dawei Wang, Fanxing Li, Liang-Shih Fan, The Ohio State University, USA

The Coal Direct Chemical Looping (CDCL) process directly converts solid fuels, like coal and biomass, into hydrogen and/or electricity with in-situ CO₂ capture by reducing and oxidizing iron oxide based oxygen carrier particles in separate reactors, without using a traditional gasifier and an energy costly air separation unit. A moving bed reducer is adopted in the CDCL process for solid fuel conversion, where oxygen carrier particles, solid fuels and enhancing gas are introduced from the top, middle and bottom sections, respectively. In order to effectively convert the solid fuels, the reducer is designed with two main stages, with the top stage for volatile conversion and the bottom section for char conversion. The volatile conversion for methane, carbon monoxide and hydrogen has been successfully tested in previous works. The char conversion in the countercurrent moving bed is studied in this work. Different operating conditions were tested for char conversion by changing the following parameters: reactor temperature, oxygen carrier flow rate, oxygen-carrier-to-char flow ratio, and enhancing gas flow rates (steam and/or carbon dioxide). Char conversion was calculated by either comparing the inlet and outlet gas flowrate difference or measuring the gas concentration at the gas outlet using a gas chromatograph. The char conversion profile at various sections in the reactor can be also retrieved by analyzing the gas composition from different sampling ports along the reactor. Oxygen carrier conversion was calculated by measuring the weight change of the carrier with a carbon analyzer. The data obtained from the bench scale unit study are analyzed and will be used for scaling up the process.

SESSION 30 Coal Science: Coal Science – 1

Fine Structure Evaluation of the Pair Correlation Function with Molecular Slice Models of the Argonne Premium Coals

Fidel Castro-Marcano, Jonathan P. Mathews, The Pennsylvania State University; Randall E. Winans, Peter Chupas, Karena Chapman, Argonne National Laboratory; Joseph M. Calo, Brown University, USA

The pair correlation function $g(r)$ is one means of evaluating the atomic spatial arrangements of coals. With coalification expectations are of limited growth in aromatic stacking and a slight growth in the aromatic cluster size over much of the

rank range. In this investigation, the pair correlation function was evaluated with molecular models of the aromatic and aliphatic portions for several Argonne Premium coals (Beulah-Zap, Illinois No. 6, Upper Freeport, Pocahontas No. 3, and non-Argonne anthracite Hon Gai) generated directly from high-resolution transmission electron microscope (HRTEM) lattice fringe images. The Fringe3D approach populates aromatic moieties matching the *distributions* of fringe: length, layers per stack, interlayer spacing, and orientations to produce a slice model of limited depth but reproducing the lattice fringe micrograph height and width. In this manner, hundreds of fringes can be duplicated rapidly and with greater accuracy than existing model construction approaches. The slice models, devoid of heteroatoms or cross-links, were utilized to predict the pair correlation function and to evaluate the fine detail of the frequency spectra. Agreement between simulated and experimental $g(r)$ functions validated the model construction approach in capturing structural features including aromatic stacking and interlayer spacing. The intensity of simulated $g(r)$ functions increases with increasing rank. The results were consistent with the expected slight increase in the stacking number observed from low- to high-rank coals with a more dramatic transition for anthracite.

Proper Blending Through PGNA Analysis

Nichelle Worthington, April Montera, SABIA Inc.; David Burton, John Hudspeth, Limestone Electric Generating Station, USA

NRG's Limestone Electric Generating Station is fed by lignite from Texas Westmoreland Coal Co's Jewett Mine. The lignite is blended with sub-bituminous coal from several mines in the Powder River Basin. It is important that the coal that is burned in the utility boiler is consistent to avoid many problems. While the PRB is usually very consistent, the lignite can vary considerably. Two PGNA analyzers were placed in parallel on conveyor belts leaving Jewett Mine on their way to Limestone Station. This gives the Station's plant operators a weight-percent measurement of the sulfur, ash, moisture and BTU in the lignite. Using this information, the operators can determine the proper blending ratios for the material. An additional PGNA analyzer was placed at Limestone Station just after blending takes place on the conveyor belt. This analyzer makes sure the proper BTU/lb has been achieved for consistent feed to the boiler. The 3 analyzers have contributed to higher efficiency, energy savings, and fewer unplanned shutdowns at Limestone Station.

Adsorption Potential of Coals and Carbon to Phenol – Thermodynamic Aspects

Boleslav Taraba, Petra Veselá, Roman Maršálek, Ostrava University, CZECH REPUBLIC

Adsorption of phenol from aqueous solutions on two samples of natural coal and one sample of activated carbon was investigated at temperatures 303 and 333 K. Adsorption isotherms were studied using batch adsorption experiments. In addition, calorimetric measurements were applied to direct determination of the adsorption enthalpy.

Markedly increased adsorption capacity to phenol was found for activated carbon, about one order exceeding these for coal samples. The shape of the adsorption isotherms for natural coals proved to follow Freundlich adsorption model, while Langmuir isotherm was confirmed as suitable model to describe phenol adsorption on activated carbon. All the samples confirmed only small change in adsorption capacity with increasing temperature. Using calorimetric examinations, enthalpy of the phenol interactions with the coals and carbon was then evaluated confirming exothermic character of the adsorption process. Based on the experimental data, principal thermodynamic parameters such as change in Gibbs energy and/or change in entropy were estimated and discussed.

Alkylation of Brown Coals and Peat by Alcohols

S. I. Zhrebtsov, Z.R. Ismagilov, Institute of Coal Chemistry and Material Science of the Siberian Branch of the RAS, RUSSIA

The fossil solid fuels (FSF), brown coal and peat bitumen are the promising sources of the wide range of valuable chemicals and products. The composition and the applications of the wax fraction of native coal and peat bitumen have been studied in the details. It is generally accepted that waxes mainly consist of mixture of fatty acids, alcohols, esters and paraffin hydrocarbons. It was recently found that the catalytic methylation of coals considerably increased the bitumens yield—substances soluble in organic solvents (methanol, hexane, and an ethanol–benzene mixture). The yield of the hexane extract which corresponds to deresined wax can be increased more than twice. The soluble products are characterized by much higher hydrogen-to-carbon ratio than that is in native coal. It is likely that this effect can be explained by high degree of depolymerization of coal matter because of the occurrence of a set of both degradation and addition reactions (coal alkylation with methanol).

This work devoted to a detailed study of changes in the composition of bitumen and, especially, the wax fraction of bitumen in the process of prealkylation of brown coals of different stage of metamorphism and peat. Alkylation of low-grade metamorphic coals and peat by alcohols in the presence of mineral and organic acids studied with using FTIR, NMR, and GC-MS. The impact of reaction conditions on the yield of extractable matter was experimentally investigated and relevant regression equations

were obtained. Changes in the group and individual compositions of the wax fractions of bitumen in the process of brown coal and peat alkylation were studied. It was found that the esters of alkylated coal waxes consisted of the native esters of fatty acids and the alkyl esters of these acids formed as a result of alkylation reaction. Esterification and transesterification were predominant among the reactions of bitumen fraction components. The positive effect of alkylation by alcohol to the increasing of the bitumen yield was found.

SESSION 31
Major CCS Demonstration Projects: General – 3

Texas Clean Energy Project Update
Barry Cunningham, Summit Power Group Inc., USA

The Texas Clean Energy Project is an integrated gasification combined cycle plant with 90% carbon capture and CCS that is being developed by Summit Power Group. The Department Of Energy awarded the project \$350M in cost matching funds in late 2009 and another \$100M in 2010. The project description and the technical aspects of how carbon is captured in the project design were presented at the 2010 Coal Conference. This proposed 2011 Coal Conference presentation will update the project's progress and the current or expected status by September 2011.

The presentation will be in Power Point format and cover the following in slide order. In the first two slides I will provide a snap shot summary of the project, its location, the DOE role, the FEED study launch and the integration of IGCC with CCS via enhanced oil recovery. In slide 3 I will give a summary of Summit Power Group Inc., and their lines of business. In slide 4 I will describe why Texas was chosen as the site of the project. Slide 5 will describe the physical site itself followed by slides with a satellite photo and a ground level photo of the site. In slide 8 I will describe the design basis for the project in broad terms and then follow with a slide showing a rendering of the facility as it will look once built. This will be followed with a number of charts showing the low air emissions of the project as well as comparisons to other recent projects in Texas. The CO₂ management process will then be described with the company Blue Source leading off take arrangements, the Texas Bureau of Economic Geology approving the MVA plan and a Carbon Management Advisory Board to advise the project on CCS. In slide 14 I will describe how Enhanced Oil Recovery provides the necessary bridge to CCS for the project. The projects plan to minimize water consumption will shared and then the rest of the presentation will provide updates on the progress of the project beginning with updates on the project's permits. I will share that the air permit was approved in early 2011 and the NEPA process EIS record of decision is expected to be issued by late summer. The FEED process will be described outlining what each entity is responsible for in terms of engineering and equipment supplied. The progress and status of the FEED process itself will be updated with completion expected by July and EPC arrangements expected to be in place by Sept. The project's chosen water supply option will be reported on with the arrangements that are in place or expected by Sept. The project's coal supply arrangements will then be updated and described as well as the status of the off take arrangements for the project's products; power, urea, sulfuric acid, argon and vitrified slag. I will conclude with the status of financing activities that are in place, or expected to be in place, that will take the project forward from engineering to construction. Currently there are 22 slide planned for the presentation.

The Purgen One Project; A Method for Full Utilization of Capital
Tim Bauer, SCS Energy, USA

The PurGen One Project is a coal gasification facility with integrated combined cycle power and urea manufacturing plants to be located in Linden, New Jersey. The project includes offshore CO₂ sequestration and a 138 mile CO₂ pipeline. The 108 acre site is a former chemical manufacturing plant site that PurGen One controls through a contract with DuPont. The site has a deepwater port as well as heavy rail access, natural gas and an adjacent electrical interconnection point. The offshore sequestration site is one that is well-characterized by over 50 exploratory wells drilled in the 1970's by major oil companies exploring off the New Jersey coast. These wells showed no hydrocarbons in the area to be used and a series of very attractive permeable layers covered by thousands of feet of impermeable material. The target reservoirs are in 300 feet of water and 8000 feet below the ocean floor. The project's feedstock will be Pittsburgh #8 coal delivered primarily by rail.

The Project began in 2007 and is currently in the permitting process. The Pre-FEED Study has been completed by Fluor. Permitting is on two basic tracks, the offshore facilities and the onshore facilities. The offshore facilities will be permitted through regulations currently under review at the US Department of Interior. The onshore facilities' permit applications are under review by the New Jersey Department of Environmental Protection. The project schedule calls for completing the FEED study and closing a construction loan financing in late 2012 with Commercial Operation in 2017.

PurGen's process design and financial structure evolved over a three year period through an iterative process designed to make full use of the large capital requirements

of IGCC projects. The basic tenets of SCS Energy's financial plan for this project are driven by a cold fact of the power industry: power plants make their money during relatively few operating hours of the year. That coupled with the equally cold fact that a project must service its debt and pay returns on equity 24 hours a day and 7 days a week create the drive for continuous rather than intermittent profitability. Many gasification projects have come to the conclusion that using synthetic gas for more than one product is an answer to the challenge of full utilization of capital. A co-product to electricity that can be stored also is a relatively obvious solution. SCS Energy believes that a vital element in a project's success is choosing the optimum co-product for each individual project. The process by which SCS Energy's PurGen One Project evolved to an electricity and urea production facility took a great deal of time, but the resulting project economics made the process well worthwhile.

**The Medicine Bow Industrial Gasification and Liquefaction Project -
Project Update**

Robert Kelly, Jon Doyle, DKRW Advanced Fuels LLC, USA

DKRW Advanced Fuels' Medicine Bow Project is scheduled for project financing within the next 12 months which would make it the first commercial scale coal to transport fuel project to be completed in the US. The project utilizes the GE gasification technology and the Exxon Mobil methanol to gasoline technology to produce regular gasoline from the coal reserve optioned to the project. CO₂ produced from the project will be liquefied and sold into the EOR market. The update will cover issues surrounding the scheduled financing and the project's newly completed (2011) CO₂ contract and the resulting impact on the CO₂ footprint of the project. The presentation will discuss the issues surrounding financing large scale coal gasification projects in the US.

Building a Cleantech USA "The New U.S. Synthetic Fuel Industry"

H. H. Graves, USA Synthetic Fuel Corporation, USA

Mr. Graves will discuss the Lima Energy project in Ohio and the Cleantech Energy project in Wyoming as examples of major synthetic fuel facilities that are moving forward and will capture 100% of CO₂ and fully utilize it in CCS and EOR. These major gasification facilities will use multiple technologies for the ultra clean btu conversion of solid hydrocarbons (renewable, biofuels, petcoke, coal) to low cost clean energy products and downstream full capture and utilization of CO₂. Both Lima Energy and Cleantech Energy have sold all of their CO₂ at the fence line on longterm contracts for downstream utilization in EOR and CCS applications. Collaboration by environmental technology interests in the U.S., Great Britain, and Canada have made this possible. This low cost clean energy platform will provide a foundation for "Building a Cleantech USA".

Demonstrating Fuel Flexibility in Commercial Operation

Fawad Khan, Francis Lau, Synthesis Energy Systems Inc., USA

Synthesis Energy Systems Inc. ("SES") enables its customers to advance gasification projects through commercial scale feedstock testing at its commercial scale coal to syngas facility ("ZZ Plant") in Zao Zhuang City, Shandong Province, China. These tests help customers affirm individual project economic viability and reduce technology risk. Included in these test campaigns have been one and two-week long continuous operations at varying loads and on widely-varying feedstock such as Chinese Inner Mongolian lignite, Chinese sub-bituminous high ash (and high friable) coal, and Australian Queensland high ash sub-bituminous coal. Through these campaigns, SES has progressed one project into the detailed engineering and construction phase and one project into the feasibility study phase. SES believes that the ability to perform these commercial scale campaigns without interruption of operation is unique to SES.

The ZZ Plant, which sells clean syngas to a neighboring methanol facility, has been in operation since early 2008 on a design coal of high ash middlings (washery wastes) from ROM bituminous coal (30-40%wt ash). SES has made significant improvements to the design, operation, and efficiency of the U-GAS®1 technology and the ZZ Plant. Included in these is the Fines Management System ("FMS"), which has demonstrated overall carbon conversion of greater than 98%. The ZZ Plant consistently demonstrates fuel flexibility and greater than 98% availability, 98% carbon conversion, and 80% cold gas efficiency.

Development of Advanced Gasification Kinetics Models for CFD (and Process Simulation) Codes

Kiran Chaudhari, Richard Turton, West Virginia University; Chris Guenther, Mehrdad Shahnam, DOE/NETL; Aytekin Gel, ALPEMI Consulting, LLC; Philip Nicoletti, Tingwen Li, URS/DOE/NETL, USA

The aim of this research is to develop detailed kinetic expressions for the gasification of a wide variety of coals and biomass that can be implemented in existing Computational Fluid Dynamics (CFD) codes such as Multiphase Flow with Interphase Exchanges (MFIx) developed at NETL, ANSYS-Fluent by ANSYS Inc. and Barracuda by CFPD Software. These expressions describe the fundamental steps taking place in the gasification of coal and/or biomass, namely, devolatilization, tar-gas chemistry, soot formation, followed by the heterogeneous and homogeneous gasification and combustion reactions. For example, the implementation of gasification kinetics in MFIx is currently achieved through a set of subroutines making up the Carbonaceous Chemistry for Computational Modeling (C3M) software. However, currently C3M has default gasification kinetics for only a few coals under a very narrow range of operating conditions.

For this purpose, the kinetic data generated through a number of detailed models such as PC Coal Lab (PCCL), Chemical Percolation Model for Coal Devolatilization (CPD), Solomon's Functional-Group, Depolymerization, Vaporization, Cross-linking model, or experimental data currently being generated at NETL will all be made available through C3M, provided the user has the necessary model licenses. This project focuses on the development of a seamless integration between PC Coal Lab, CPD and Solomon's model through C3M to leading multiphase CFD solvers. The C-3M graphical user interface (GUI) is designed to allow users to exercise the various kinetic models to evaluate graphically the effect different fuels and/or gasifier operating conditions have on gasification kinetics. Users can evaluate rates and yields of different kinetic models through the GUI or compare these predictions to their own in-house experimental information. The C3M GUI allows multiphase CFD users to make an informed decision on the set of kinetics to use in gasifier simulations. Furthermore, the C3M GUI will allow the multiphase CFD user to select kinetic information from a particular kinetic model and have that information properly formatted and seamlessly integrated into the CFD input files ready for immediate use. In this study, the development, status, and future development of C3M will be discussed along with current gasifier applications leveraging the C3M software.

Numerical Analysis of Gasification Performance via Finite-Rate Model in a Cross-Type Two-Stage Gasifier

Yau-Pin Chyou, Yan-Tsan Luan, Institute of Nuclear Research, Atomic Energy Council, TAIWAN; Ting Wang, University of New Orleans, USA

The gasification process in the E-Gas like gasifier through computational analysis is investigated in this paper by using the commercial software, ANSYS FLUENT. The studied E-Gas like gasifier is a pressurized, oxygen-blown, entrained-flow reactor. The 3D steady-state Navier-Stokes equations are solved in an Eulerian-Lagrangian frame of reference. All the coal particles are treated as a discrete second phase dispersed in the continuous phase via the Discrete Phase Model (DPM) with the stochastic tracking to consider the turbulent dispersion effect. Eight species transport reactions, consisting of combustion, gasification, volatiles cracking, and water-gas-shift reactions with assigned reaction rate constants, are solved through the Finite-Rate/Eddy-Dissipation Model.

This paper investigates the effects of the coal slurry concentration, O₂/Coal ratio, 1st-2nd fuel distribution ratio, and coal particle size on the gasification performance. The outlet species composition, syngas heating value, carbon conversion efficiency, and cold gas efficiency are used to evaluate the gasification performance. The results show that the preliminary gasification process is successfully modeled and the syngas composition and temperature have an acceptable consistency with the results published in DOE/NETL report. The global chemical reactions are shown to be strongly affected by the finite rates. The study of varying operating parameters shows that the increased O₂/Coal ratio results in the decrease of CO and the increase of CO₂ and exit temperature. After modifying the rate constant of water-gas-shift reaction, it can be found that as the coal slurry concentration increases, the mass flow rate of H₂, CO₂ and H₂O increase while that of CO decreases. The increased particle size leads to lower CO, H₂O and exit temperature, but higher H₂ and CO₂. With a fixed total coal slurry flow rate, increasing the 2nd stage coal feeding results in more CO₂ and H₂ but less CO, H₂O and exit temperature. The overall results show that the present CFD and reaction models can adequately capture the gasification behavior inside the gasifier; however further efforts should be made to achieve more precise prediction and advanced analyses in the future.

A mild gasification concept has been developed to provide an innovative approach to retrofitting existing pulverized coal power plants to enhance their efficiencies and reduce their emissions. The objective of this study is to develop a numerical model to investigate the thermal-flow and gasification processes inside a specially designed fluidized-bed mild gasifier using the commercial CFD solver ANSYS/FLUENT, employing the Eulerian-Eulerian method for both the primary phase (air) and secondary phase (coal particles). However, the Eulerian-Eulerian model in the existing code does not facilitate any built-in devolatilization model. As such, a model has been developed for devolatilization along with demineralization. The Navier-Stokes equations and seven species transport equations are solved with three heterogeneous (gas-solid) and two homogeneous (gas-gas) global gasification reactions. Development of the complete model starts from adding demineralization first, then devolatilization, and then adding each chemical equation one at a time. The simulation model has been successfully developed. The results are reasonable but require future experimental data for verification.

Progress on a New Integrated 3D UCG Simulator and Its Initial Application to Modeling Previous Field Tests

John J. Nitao, David W. Camp, Joshua A. White, Gregory C. Burton, Mingjie Chen, Thomas A. Buscheck, Lawrence Livermore National Laboratory, USA

At the 2010 PCC conference, we described (Nitao et al., 2010) a comprehensive simulator that is being developed for supporting underground coal gasification (UCG) design and operation. Our ultimate goal is to have a simulator that can model all of the following processes:

- Coal gasification and gas reactions, heat and mass transfer taking place next to the cavity wall
- Boiling of in-situ water
- Spalling of coal and rock from the cavity wall
- Coal gasification, gas reactions, mass and heat transfer in the rubble material
- Cavity gas flow and reactions leading to prediction of gas outflow composition
- Cavity gas heat transfer by advection, conduction, and radiation
- Wall deformation, roof collapse, and subsidence in response to cavity growth
- Seepage of water into the cavity
- Effect of aquifer dewatering operations
- Effect of aquifer drawdown on subsidence
- Rubble zone surface material settling
- Transport of contaminants
- 3D geometry of cavity and rubble surface progression

This simulator is expected to help answer important questions, such as:

- What are the characteristics of a good site?
- How do we characterize a site?
- How do we operate UCG?
- What is the proper strategy for injection rates and its gas composition?
- What is the best injection/extraction well spacing?
- What is the maximum spacing between modules that maintains overburden integrity?
- How do we locate and operate dewatering wells?
- How do we monitor UCG?
- What is the environmental impact?

Simulation of UCG is not only challenging because it involves a tremendous variety of coupled physical/chemical processes, but many of these processes occur over vastly disparate space and time scales. Substantial progress has been made to the simulator within the past year to overcome these challenges. The current system includes a preliminary integration of the following modules:

- Wall Zone Module – the 1D wall model is finished and multiple 1D wall zone models are now located on the cavity wall to model coal gasification and in-situ water evaporation.
- Rubble Zone Module – a 0D lumped parameter representation. This is currently being extended to a 3D reactive porous flow and transport model.
- Cavity Gas Module – a simplified 1D reactive transport model. This is currently being extended to include a higher dimensional CFD model.
- Geomechanics Module – an existing geomechanics code called Geocentric has been integrated to model formation deformation and roof collapse. This integration is currently being enhanced to include subsidence, including the effect of water table changes.
- Hydrology Module – an existing hydrology code called NUFT has been integrated to model seepage into the rubble zone and open cavity. The

integration will be enhanced to include the effect of geomechanical porosity changes on formation permeability.

We have applied this simulator to modeling a field test that took place in the 1980's. It was selected because of the extensive data that is readily available. Comparisons are made between model predictions and field data including: cavity growth and geometry, gas composition, roof collapse events, and in-situ temperature measurements. Plans for future development and research directions are given.

Reference

John J. Nitao, Thomas A. Buscheck, Souheil M. Ezzedine, S. Julio Friedmann, and David W. Camp (2010), An integrated 3-D UCG model for predicting cavity growth, product gas, and interactions with the host environment, 27th Ann. Pittsburg Coal Conf., Istanbul, Turkey, Oct. 11-14, 2010.

SESSION 33 Coal-Derived Products: General – 6

A Sustainable and Reliable Approach to Ash Monofills Closures Using Structured Membrane and Synthetic Turf

Lindsey A. Turtle, Agru America; Mike Ayers, ClosureTurf; Jose Urrutia, Riley, Park, Hayden and Associates, Inc., USA

As a response to numerous failures and poor performance of environmental closures at landfills and ash monofills, engineers have looked at new approaches in establishing a more physically stable and environmentally sound solution. Traditional waste closures require large amounts of soil for their construction, and many experience on-going erosion and sedimentation issues. Traditional covers are highly reliant on trucking soils, heavy civil construction and on-going maintenance and repairs in order to maintain their integrity. New methods are needed to lower the impact on the environment throughout the capping construction process.

A potential solution to landfill closure failures and construction and operation environmental impacts has been the implementation of exposed geomembranes. However there are disadvantages to these systems such as: accessibility, lack of membrane protection, wind uplift issues and aesthetics. The latest approach presented here builds off of the success of using exposed geomembranes with a number of improvements to address the disadvantages of exposed systems. This system incorporates high interface friction materials, and multiple layers of protection provide by a turf system. The system is ballasted with sand infill to provide wind resistance and accessibility. Like other exposed membrane caps there is no soil and vegetative layer. This system also provides for a stable and rapid installation that allows for the reduction of emissions at earlier phases of development.

Rapid Coal Pyrolysis to Acetylene in Multi-Stage Thermal Plasma Reactor

Yi Cheng, Binhang Yan, Yong Jin, Tsinghua University; Cliff Y. Guo, Xuan Li, Changning Wu, National Institute of Clean-and-low-carbon Energy, CHINA

Using thermal plasma for coal pyrolysis to acetylene provides a direct route to make chemicals from coal resources, where the temperature field in the reactor plays a dominant role in the performance of coal devolatilization. A comprehensive computational fluid dynamics with discrete phase model (CFD-DPM) has been established to describe the rapid coal pyrolysis process in a reactor under ultra-high temperatures. The simulations based on this model helped to understand the complex gas-particle reaction behavior in the millisecond process of coal pyrolysis. The particle-scale physics such as the heat conduction inside solid materials, diffusion of released volatile gases, coal devolatilization, and tar cracking reactions were incorporated. The improved chemical percolation devolatilization (CPD) model was applied to describe the devolatilization behavior of rapidly heated coal based on the physical and chemical transformations of the coal structure. This model was proved to be qualified for describing the complex gas-particle reaction behavior with milliseconds residence time by the operation experience of a 5-MW plasma reactor.

Then the simulations revealed the fact that the particle heating and devolatilization are strongly affected by the appropriate grade of the temperature and the residence time of coal particles staying in the temperature zone(s). Too concentrated energy input in the reactor may not intensify the reactor performance. As a potential solution, multi-stage heating design would provide more flexibilities to effectively adjust the devolatilization performances under the same total amount of energy input.

SESSION 34 Carbon Management: SECARB-ED CCS Training Session – 2

Water in Carbon Capture and Sequestration: Challenges and Opportunities

James W. Castle, John H. Rodgers, Jr., John R. Wagner, Clemson University; Gerald R. Hill, Southern States Energy Board, USA

Carbon capture and sequestration (CCS) technologies have the potential to greatly reduce anthropogenic carbon dioxide emissions to the atmosphere. The CCS process involves capture of CO₂ gas generated at large stationary sources such as thermoelectric power plants followed by compression and then transport to geologically favorable areas where the captured CO₂ is injected into subsurface units such as depleted oil and gas reservoirs, deep saline formations, or unminable coal seams. Water issues associated with CCS present both challenges and opportunities. Increased demand for water will be driven by implementation of capture systems at power plants and other carbon sources, and water will be produced at sequestration sites. Because water consumption is estimated to increase by 50 to 90% with the addition of CO₂ capture and compression using existing technologies (USDOE, 2009), new sources of water supply and augmentation of existing supplies will be needed. Although water production may not be necessary during injection of CO₂ into geologic units for long-term sequestration, water production may be advantageous to increase storage volume and reduce pore pressure. Opportunities for beneficial use of sequestration produced waters (SPWs) will occur if energy-efficient and cost-effective treatment technologies are identified and implemented.

Possibilities for beneficial use of SPWs include power-plant cooling and other industrial uses, irrigation, livestock watering, augmentation of surface water flow, and re-injection for pressure maintenance or waterflooding of oil and gas reservoirs. However, SPWs may contain constituents of concern that require treatment prior to use. The potential for beneficial use of a specific SPW can be assessed by characterizing the SPW in terms of quantity and quality, including both chemical and biological risk, and comparison with criteria or guidelines for various uses. Quantity and quality of SPWs vary with type (i.e. depleted oil and gas reservoirs, deep saline formations, or unminable coal seams) and are site-specific. Water characterization studies have demonstrated that waters produced from oil and gas reservoirs and from coal seams contain a wide range in type and concentration of cations, anions, and organic compounds. Deep saline formations contain water having a concentration of total dissolved solids exceeding 10,000 ppm (USEPA, 2008). Treatment technology for a specific SPW should be selected based on water characteristics and intended use. For example, constituents that could cause scaling, corrosion, or biofouling require treatment prior to industrial use, such as in a power plant. Existing technologies with potential application to treating SPWs include reverse osmosis, thermal desalination, electrodialysis, freeze/thaw, and constructed wetland treatment systems. Preferred technologies will be those that provide effective treatment with a low energy demand. A range of treatment options is likely to be implemented for SPWs because of differences from site-to-site in water quantity and quality and potential use.

Clean Coal Technology Development and its Impact on the Energy Industry in the Southeastern United States

Jack Pashin, Geological Survey of Alabama, USA

Clean coal technology development constitutes a diversity of efforts to increase the efficiency of electricity generation while reducing environmental impact. Early efforts focused on reducing the output of particulates, SO_x, and NO_x into the atmosphere and were successful at improving air quality during major industrial expansion. Where these technologies are being applied in developing nations, the improvement of air quality is obvious and immediate. Current efforts in the United States are focused on greenhouse gas mitigation and the development of carbon capture and storage technologies. Carbon capture technology can provide abundant CO₂ suitable for enhanced oil and gas recovery and thus creates potential for a new synergy between electricity generation and petroleum production.

In the southeastern United States, clean coal technology development includes the design and construction of a 25-Mw CO₂ capture facility that can be integrated into pulverized coal plants and a coal gasification plant with pre-combustion capture. Testing of geologic carbon storage in mature oil reservoirs, coal, and saline formations has verified the injectivity and capacity of the major carbon sinks and has been instrumental in developing and implementing reservoir monitoring technology. New exploratory wells are being drilled at power plants, and ongoing field tests are focused on large-scale injection of carbon dioxide into mature oil reservoirs and saline formations. Results to date indicate that CO₂ injection can increase oil recovery by about 15% of original oil in place in candidate fields and can increase coalbed methane reserves by more than 20%.

CO₂ Sequestration in Unmineable Coal with Enhanced Coal Bed Methane Recovery: The Marshall County Project

James E. Locke, Richard A. Winschel, CONSOL Energy Inc.; Richard A. Bajura, Thomas H. Wilson, Hema J. Siriwardane, Raj Gondle, Henry Rauch, Brad Hega, Shahab D. Mohaghegh, West Virginia University, USA

A pilot test is being conducted in Marshall County, West Virginia, USA, to evaluate enhanced coal bed methane recovery and simultaneous carbon dioxide sequestration in an unmineable coal seam in the Northern Appalachian Basin. Injection of carbon dioxide (CO₂) began in September 2009 and it continues at the time of this writing. This paper describes the project and its current status and summarizes recent work by the research collaboration.

China Coal and Carbon Capture and Storage (CCS)

Timothy R Carr, West Virginia University, USA

China high economic growth has created various challenges due to rapidly increasing energy requirements. These include net energy import dependence, domestic environmental pollution and ecological destruction, cross-border pollution, and a rapid increase in the contribution to global CO₂ emissions. The continued growth of the economy will amplify these challenges. China is and will remain largely dependent on coal as the major domestic contributor for its long-term energy requirements. Although energy consumption on a per country basis is approximately equal to the United States, coal comprises 70 percent of total energy input compared to approximately 25 percent in the US. In addition the increase demand for coal has resulted in China becoming a net coal importer during 2009. Coal consumption in China is forecasted to continue to increase from approximately 3 billion metric tons in 2010 to approximately 4 billion metric tons in 2030, and it is expected to remain above 60 percent of the total through 2020. This dependence on coal and rapid economic growth has resulted in China exceeding the US as the largest and fastest growing contributor to greenhouse gas.

Several projects are underway to broaden the use of coal and to manage CO₂ emissions through the commercial-scale demonstration of carbon capture and storage (CCS). These projects include GreenGen, a consortium of China's largest power and coal companies, that is building a coal-based power generation system with hydrogen production through coal gasification, power generation from a combined-cycle gas turbine and fuel cells. The project is slated to begin capture of a slipstream of CO₂ in 2013 and full-scale capture scheduled in 2017. Efforts are also underway to construct an Oxy-Fuel power plant in Shanxi Province with CCS. In Inner Mongolia, China Shenhua Coal Liquefaction Company (CSCLC) has developed the world's first modern direct coal liquefaction (DCL) facility. When in full production, this plant will produce significant very large quantities of CO₂. While the plant was designed and built prior to the current emphasis on carbon management, it is now the goal of CSCLC to capture and permanently store much of this CO₂ in geologic formations in the Ordos Basin.

We have been working with our Chinese colleagues to undertake several resource assessments of potential geologic storage sites that are associated with these projects. The primary findings and recommendations highlight the geologic, organizational and economic challenges. However, the initial results indicate that the proposed geologic storage opportunities deserve further study and CCS in China coupled with new creative approaches of coal use appear to be both feasible and desirable.

Public Outreach and CCS: A Critical Analysis

Brad Kelley, Nino S. Ripepi, Virginia Center for Coal and Energy Research at Virginia Tech, USA

After participants have listened to several technical, scientific, and engineering presentations on CCS, I will close with a brief presentation on some recent directions in public outreach for CCS. As it is worthwhile considering and occasionally reconsidering, without broad public support, none of this gets done; no money gets appropriated and projects come to a halt. After attending recent outreach sessions at CCS conferences and reading recent published papers and documents, I am convinced that a critical analysis of public outreach is needed. Though I will advocate a certain view (outside of what I will define as the mainstream view of public outreach for CCS), the point is to identify certain options and be aware of the philosophical implications and commitments of each. CCS is something many here believe in, but we have to be able to take our case to the public, honestly, with the strongest arguments and best evidence we have. Participants here share a belief that CCS is of critical importance for the future of energy and for sound energy policy, so it is crucial that we all understand those arguments in a way that can be taken to the public with confidence and integrity.

SESSION 35 Combustion: Chemical Looping – 2

Alstom's Calcium Oxide Chemical Looping Prototype, Program Update

Paul R. Thibeault, Herbert E. Andrus, Jr., John H. Chiu, Carl D. Edberg, Alstom Power Inc.; Bruce Lani, DOE/NETL, USA

Alstom Power Inc. is developing a Chemical Looping Process, utilizing Calcium Oxides as oxygen carriers to transport oxygen from air to the fuel, which has the potential to capture CO₂ from new and existing coal-fired power plants while maintaining high plant power generation efficiency. This new power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. The chemical and thermal looping technology could also be potentially configured as a hybrid combustion-gasification process producing a syngas or hydrogen for various applications while also producing a separate stream of CO₂ for use or sequestration. Development of the process has progressed through three phases and is currently in Phase IV, which will concentrate on designing, building and testing a 3 MWth prototype of the Chemical Looping process that will integrate all of the equipment and systems required to operate the facility. Operation of the facility will be used to characterize performance and develop design information for future plants.

Work in Phase I and Phase II validated the chemistry required for the Chemical Looping process, while work in Phase III investigated the solids transport mechanisms and design requirements. In Phase IV, construction of the prototype has been completed and shakedown has been done. Testing in the prototype has started. In addition, a cold flow model of the prototype has been constructed and successfully operated. The cold flow model data is used to predict operating conditions for the prototype and help in operator training. This project was funded by the DOE / NETL's Innovations for Existing Plants (IEP) Program.

Iron Based Chemical Looping Processes Developed at The Ohio State University

Deepak Sridhar, Liang Zeng, Andrew Tong, Rae Kim, Zhenchao Sun, Siwei Luo, Liang-Shih Fan, The Ohio State University, USA

The chemical looping processes (CLP) have the potential to efficiently utilize the indigenously abundant carbonaceous fuels such as coal in an environment-friendly manner. The CLP utilize an oxygen carrier particle to indirectly convert carbonaceous fuels while capturing the CO₂ byproduct for sequestration. This attractive incentive has resulted in global development of the chemical looping technology. At the Ohio State University, multiple chemical looping efforts ranging from pre-combustion to post-combustion of coal have been demonstrated under various scales. The iron-based CLP developed at the Ohio State University (OSU) presents a unique advantage compared to the other chemical looping technologies. The combination of a moving bed reactor system with the use of iron-based oxygen carrier results in the potential generation of high purity H₂. This makes the iron-based CLP a fuel and product flexible technology. The OSU CLP can be classified into Syngas Chemical Looping (SCL) and Coal-Direct Chemical Looping (CDCL) technologies based on the fuel type handled in the looping system. The SCL process is tailor-made for complete conversion of any carbonaceous gaseous fuel like syngas and natural, with 100% in-situ CO₂ capture. The process can be configured to generate H₂, electricity or any combination thereof. It can also be incorporated into the Fischer-Tropsch process to enhance the efficiency and yield of coal to liquid fuels production. The process has been tested under a 25kWth sub-pilot scale continuous operation for more than 100 hours with current efforts focused on the scale up demonstration of the 250 kWth pilot SCL unit. The CDCL process involves the direct utilization of solid fuels, such as coal, biomass, etc., in the chemical looping reactor system with the same product flexibility as the SCL process. The direct introduction of solid fuel (coal) into the reactor system provides improved efficiency while presenting unique challenges. The CDCL system has been extensively demonstrated in the bench-scale (2.5 kWth) and the sub-pilot scale (25 kWth) unit is currently being constructed.

This presentation will discuss multiple aspects of the CLP being developed at OSU. The process reaction scheme of both the SCL and CDCL process will be presented in detail. This will be followed by the techno-economic evaluation of both the processes with a comparison to the conventional state-of-the-art processes. The results obtained in the SCL sub-pilot demonstration unit will be summarized followed by the preliminary CDCL testing results. The robust performance of the iron oxygen carrier particles synthesized at OSU will be highlighted with emphasis on future pathway for improvement. The challenges that need to be addressed for the SCL and CDCL processes will be elaborated. Finally, the scale-up strategy of the processes for commercial use will also be highlighted.

Comparative Investigation on Chemical Looping Combustion of Coal-Derived Synthesis Gas Containing H₂S Over Supported Bimetallic Fe₂O₃-MnO₂ and Fe₂O₃ - CuO Oxygen Carriers

Ewelina Ksepko, Marek Sciazko, Institute for Chemical Processing of Coal, POLAND; Hanjing Tian, Thomas Simonyi, Parsons; Ranjani V. Siriwardane, DOE/NETL, USA

The paper contains results on promising combustion technology known as chemical looping combustion (CLC). The objective of paper was to prepare supported bimetallic Fe₂O₃ - MnO₂ and Fe₂O₃ - CuO oxygen carriers and to evaluate the performance of these for the CLC process with synthesis gas/air. Thermo gravimetric analysis (TGA) were conducted to evaluate the performance. Multi cycle tests were conducted in an atmospheric TGA with oxygen carriers utilizing simulated synthesis gas with & without H₂S. Effect of H₂S impurities on both the stability and the oxygen transport capacity was evaluated. Chemical phase composition was investigated by X-Ray diffraction (XRD) technique.

Five Cycle TGA tests at 800 °C indicated that all oxygen carriers had a stable performance at 800 °C. It was interesting to note that there was complete reduction/oxidation of the oxygen carrier during the 5-cycle test. The fractional reduction, fractional oxidation and global reaction rates of the reactions were calculated from the data. It was found, that support had a significant effect on both fractional reduction/oxidation and the reaction rate. The oxidation reaction was significantly faster than the reduction reaction for all oxygen carriers. The reaction profile was changed by the presence of H₂S but there was no effect on the reaction rate due to presence of H₂S in syntheses gas.

Quantitative Rate Analysis of Experimental Data Relevant to Chemical Looping with Oxygen Uncoupling

JoAnn S. Lighty, Asad H. Sahir, Adel F. Sarofim, Hong Yong Sohn, University of Utah, USA

The development of solid fuel combustion technologies which incorporates economic capture of CO₂ in coal fired power plants is a challenge that is being actively tackled by researchers. Chemical Looping with Oxygen Uncoupling (CLOU) is a variant of the Chemical Looping Combustion (CLC) process which is a promising candidate to achieve the aforesaid objective. Enhanced reaction rates (45-50 times greater) for combustion of solid fuels have been reported in experimental studies on CLOU in comparison to conventional CLC. This increase in reaction rates is attributed to the combustion mechanism in CLOU, where the solid fuel introduced burns directly in the presence of gaseous phase oxygen released by the decomposition of a circulating metal oxide (e.g. CuO). In contrast, conventional CLC necessitates gasification of solid fuels to synthesis gas which is subsequently oxidized by the circulating oxygen carrier.

In this talk an interpretation and analysis of the reported literature studies on CLOU will be presented. The processes occurring in CLOU shall be explained with the help of developed mathematical models which take into account chemical kinetics and mass transfer effects.

Modeling, Simulation and Advanced Controls for Prototype Chemical Looping Process

Abhinaya Joshi, Xinsheng Lou, Carl Neuschaefer, Alstom Power Inc., USA

Alstom Power Inc. (Alstom) is collaborating with the U.S. Department of Energy (DOE) in a project developing an entirely new, ultra-clean, low cost, high efficiency power plant technology for the global energy market. This new power plant concept is based on a process utilizing high temperature chemical and thermal looping technology. This chemical looping (CL) technology can be configured as a next generation power plant with a controlled stream of CO₂ for use or sequestration.

In coordination with the process development, Alstom is developing advanced sensors and controls for this chemical looping system under a DOE advanced research project co-sponsorship. A key part of this controls development is a new computational approach to process dynamic simulations for use in the control development. The Phase I controls development focused on developing an early understanding of the basic transport processes and the underlying process control dynamics. The effort included characterization of the chemical looping process, building solid transport process math models, and developing offline and real-time dynamic simulation models and software to support control investigations. These first-of-a-kind (FOAK) dynamic simulators in conjunction with Alstom's experimental facilities were used to explore advanced controls concepts such as model predictive control (MPC) for application to the chemical looping process. Papers were presented at IPCC 2009 and IPCC 2010 summarizing the progress of the Phase I R&D project executed by Alstom Power. With a 3MWth prototype scale CL facility under development by the end of Phase I, a small Phase I controls project scope was extended in order to enable a smooth transition from the Phase I project (simulation and controls of the experimental scale process) to a future proposed Phase II project (scale-up CL prototype process - 3MWth). Efforts focused on preparations for the scale-up modeling, simulation and control specification development for the 3MWth CL prototype.

This paper presents recent progress achieved by Alstom on process characterization, modeling and development of dynamic simulation, and advanced control designs for the 3MWth prototype CL process. First, the paper introduces the technology

background and project status. Then, the paper presents the technical approach to first principle modeling of a multi-loop reaction flow model, model discretization, and software and numerical simulation development. The simulation results and numerical problems resolved during the computational studies are presented at a proper technical level. Next, the paper shares the design and test results obtained so far from investigations of closed-loop PID controls and model predictive control (MPC). Operational process optimization along with advanced controls has been established as a key for this future clean power generation plant. Finally, this paper explains future planned development of integrated control and optimization along with Alstom's Chemical Looping technology development for clean fossil power.

Study the Effects of Hydration on the CO₂ Adsorption Capacity of Calcium-Based Sorbents with Density Functional Theory Calculation

Siwei Luo, Fuchen Yu, L.-S. Fan, The Ohio State University, USA

Hydration is known to improve the reactivity and CO₂ absorption capacity of Calcium-Based CO₂ sorbents, which are frequently used in the CO₂ sorbent based chemical looping processes such as the Carbonation-Calcination Reaction (CCR) process. In this article, the physical characteristics of CaO sorbents before and after hydration are examined using SEM and XRD techniques. It was determined that hydrogen promotes the formation of (100) plane, which can play an important role to the performance of the sorbent. In order to further explain the experimental results, density functional theory (DFT) calculation are performed to illustrate the behavior of CO₂ adsorption on the CaO surface and its subsequent transformation to CaCO₃. Three dominating planes on the CaO surface, i.e. CaO(100), CaO(110) and CaO(111), are considered in the calculation. For all three surfaces, CO₂ molecule can be stably adsorbed with the C atom adjacent to the O lattice sites in CaO and the O atom in CO₂ pointed towards the Ca lattice sites. DFT results also indicate that CO₂ adsorption is more favored on a CaO(110) surface compared to CaO(111) surface and CaO(100) surface. The strong physical adsorption of CO₂ on CaO(110) surface, however, inhibits the subsequent formation of CaCO₃.

SESSION 36 Coal Science: Coal Science – 2

Influence of Discard Mineral Matter on Slag-Liquid Formation and Ash Melting Properties of Coal - A Factsage™ Simulation Study

JC van Dyk, MJ Keyser, Sasol Technology R&D, SOUTH AFRICA

The ash fusion temperature (AFT) profile of a coal is one of the parameters currently widely used in coal marketing and utilization to assess coal ash fusibility and melting characteristics, and to predict the melting behaviour of the coal ash in coal conversion processes. However, the flow temperature of a specific coal source alone does not provide enough insight into the slag formation behaviour at temperatures below the flow temperature. It has been demonstrated that ash flow temperature can be correlated with FACTM equilibrium calculations, and that such equilibrium calculations provide useful information regarding the phase transitions that take place well below the final ash flow temperature as indicated by a standard AFT analysis.

The overall objective of this study is to use the properties of different types of mineral matter and to simulate the effect on slag-liquid formation and ash flow temperature for individual mineral types as well as blends. A thermo-equilibrium simulation approach based on FACTSAGE™ was applied.

The slag-liquid flow temperature simulations for coal and individual mineral types compared favourably with the actual measured ash flow temperature and are within the experimental error of an AFT analysis (±30°C). The slag formation of coal showed a more gradual increase in the amount of slag formed over a temperature compared to specific individual mineral types. This can be explained by the ash composition of coal which has a more even distribution of minerals compared to mineral types that have a significantly high SiO₂ or CaO content respectively. From this result it is also confirmed that flow temperature properties are non-additive and cannot be calculated from a weighted average principle. It was shown by FACTSAGE™ modelling that the addition of a discard blend to this specific coal source will have no significant effect on the flow temperature of the blend. The FACTSAGE™ modelling showed that the amount of slag-liquid of the ash that was studied is highly dependent on the temperature to which the ash is exposed. For example, the amount of slag-liquid can double by only increasing the operating temperature of a process within a small window of as little as 100°C. This could explain why coal conversion processes such as combustion, entrained flow gasification, etc. can experience periods of unstable operation despite an apparent constant feed coal quality being observed with very little variation in ash flow temperature. The important parameter is thus not the actual flow temperature, but rather the amount of slag formation at a specific operating temperature.

The inability of the standard AFT analysis to reflect changes in ash melting behavior with relatively small variations in ash composition was highlighted in this study. Even though variation in mineral matter content of the coal blend may have limited or no effect on the actual ash flow temperature, it can significantly change the amount of

slag present in the ash bed. The variation in operating temperature can also result in a significant change in slag formation (positive or negative) which is not always reflected by the standard AFT analysis method.

It is concluded that FACTSAGETM thermodynamic modelling of ash melting behavior provides a method to address the shortcomings of the standard AFT determination, which can add significant value and insight towards the improvement of the operational stability of coal conversion processes such as combustion and gasification.

Coal It's Elementary My Dear Watson

Jonathan P. Mathews, Vijayaragavan Krishnamoorthy, Enette Louw, Aime H. N. Tchappa, Fidel Castro-Marcano, Vamsi Karri, Dennis A. Alexis, Gareth D. Mitchell, The Pennsylvania State University, USA

The spatial arrangement and abundance of the elements: C, H, N, O, S often correlate or directly influence a plethora of coal properties. For >90 years, attempts have utilized the ultimate (elemental) analysis of coal to predict a wide variety of properties such as: calorific value (higher heating value), volatile matter, vitrinite reflectance (max maximum), Hardgrove grindability index, helium density, aromaticity, etc. While many relationships resulted in graphical plots that have utility even today, numerical values can also be directly calculated utilizing the correlations. These have the potential to allow rapid predictions and low-cost approaches to coal property determination. Here the many correlations addressing multiple coal properties were reviewed and where possible evaluated against the Pennsylvania State University Coal Sample Bank and Database for vitrinite-rich (>80% by point counting) United States Coals. Around 40 correlations were found. While some correlations, such as calorific value predictions are accurate over a wide range of compositions, others are challenged to capture the predictive value accurately, over a wide range, but may capture the trends.

Full-Scale Mercury Control Demonstrations: ICR Sampling with Mercury Control

Jason Laumb, John Kay, Energy & Environmental Research Center, University of North Dakota; Mark Thoma, Otter Tail Power Company, USA

The U.S. Environmental Protection Agency (EPA) issued an information collection request (ICR) for all coal- and oil-fired utility units of >25 MWe. This information will assist in the formation of a maximum achievable control technology standard for mercury.

The Otter Tail Power Company's Hoot Lake Plant Unit 2 was one of 50 randomly selected plants by EPA to perform Part III emission data for all hazardous air pollutant (HAP) groups except dioxin/furans. Otter Tail Power was not only to provide the required general facility information, fuel analyses, and emission data but was also randomly selected to provide data on all HAPs groups as defined in ICR Part III. This project provided the opportunity to assist Otter Tail Power with the ICR requirements and collect data on the effect of a mercury control technology on the emissions of selected HAPs.

Comparison of the data with the identical sampling conducted during the ICR portion of the project agreed with past work in that the resultant concentrations of HAPs were highly variable. The testing indicated that the majority of metallic HAPs did not change except for beryllium and cobalt, which did decrease, and selenium, which greatly increased. The results of all HAPs measurements will be included in the presentation.

Mercury Speciation and Emission from Pilot-scale PC Furnaces under Air- and Oxy-fired Conditions

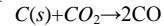
Brydger Van Otten, Andrew Fry, Brad Adams, Reaction Engineering International; Larry Bool, Praxair Inc., USA

Mercury in oxy-combustion systems equipped with CCS is of concern for manufacturers of flue gas cleanup and compression equipment. Significant material degradation occurs as mercury readily amalgamates with aluminum heat exchangers. The speciation and behavior of mercury in oxy-combustion systems must be understood before a mercury removal system can be developed. Experiments were carried out in University of Utah's 1.5 MW and 100 kW pulverized coal furnaces and a 200 kW circulating fluidized bed. For these experiments, a Utah bituminous coal was fired with either air or oxygen. Mercury measurements were performed on the flue gas, coal and ash. The mercury mass balance for these experiments ranged between 85-112% with the exception of the 1.5 MW oxy-fired case, which included flue gas recycle. Native mercury removal in the three systems was higher for all oxy-fired cases, most likely due to elevated carbon in ash. Mercury removal increased from 83% to 87% in the CFB, from 16% to 84% in the 1.5 MW furnace (most likely due to filter cake interaction of the flue gas recycle stream) and from 61% to 77% in the 100 kW furnace. Speciated flue gas measurements were performed on the 1.5 MW furnace and the CFB. Little difference in flue gas mercury speciation was seen between the air- and oxy-fired conditions. Mercury oxidation in the CFB was 29±9% under air-fired conditions and 24±11% under oxy-fired conditions. In the 1.5 MW furnace, mercury oxidation was 55±7% under air-fired conditions and 59±6% under oxy-fired conditions.

The Effect of the Boudouard-reaction on Reaction Rates of Coal Chars in CO₂/O₂- and N₂/O₂-Atmospheres at Oxygen Contents from 0% to 30%

Dominik Christ, Malte Förster, Reinhold Kneer, M. Habermehl, O. Hatzfeld, RWTH Aachen University, GERMANY

The reactivity of coal chars made from Rhenish brown coal is studied using a lab-scale fluidized bed reactor. In order to determine the effect of the gas phase in oxyfuel conditions, experiments have been conducted in both in CO₂/O₂ and N₂/O₂ atmospheres. Oxygen content was varied between 0 mole-% and 30 mole-%. In CO₂/O₂ conditions at 0% O₂, the pure Boudouard reaction



is measured. The temperatures of the experiments were 1073 K and 1273 K, respectively. The observed reaction rates are presented. Furthermore, the influence of the different transport properties in mixtures of CO₂/O₂ and N₂/O₂ is calculated. The results show that though the diffusivity is lower in CO₂/O₂ mixtures, the resulting mass transfer coefficient is higher. Using the mass transfer coefficient, global kinetic rates of the surface reaction and the order of reaction *n* regarding O₂ are determined. The results show *n*<1 for the studied conditions.

SESSION 37

Major CCS Demonstration Projects: General – 4

FutureGen 2.0 Oxy-Combustion Repowering at Meredosia

Steve Moorman, Babcock & Wilcox, USA

FutureGen 2.0 (FG2) is a DOE-sponsored program designed to prove a near-zero emissions coal-based power plant concept by 1) repowering a 202 MWe unit with oxy-combustion at an Ameren power station in Meredosia, Illinois, 2) capturing CO₂ from the repowered oxy-boiler and 3) transporting the CO₂ from Meredosia to a geologic CO₂ sequestration repository. This presentation will provide an overview of the oxy-combustion process, describe the FG2 oxy-boiler and flue gas quality control system equipment design and plant arrangement and will provide a general overview of the operation of the boiler and flue gas clean-up equipment. The CO₂ capture and CO₂ transport/sequestration aspects of FG2 will be covered in separate but complementary presentations given by Air Liquide and the FutureGen Alliance, respectively.

Air Liquide's Global Roadmap Toward the Industrialization of Oxy-Combustion

Roger Gilchrist, Mark Estopinal, Etienne Sturm, Jerry Oliver, Air Liquide Engineering & Construction, USA

Recent events in the nuclear industry have further exacerbated the global struggle between demand for energy and concern over the environment. While the debate rages over wind, solar and renewable energy, most experts agree that these resources can only provide a very small percentage of the world's energy needs. Reduction in energy demands through conservation and avoidance has and will continue to help, but the growing global need for energy in emerging economies have dwarfed those impacts. The industry is left with very little choice but to continue to use coal and natural gas. With 84% of the energy that keeps America stable coming from oil, gas, and coal, clean energy is essential no matter the source. Clearly, leaders like Dr. Steven Chu, Secretary of Energy, believe coal is a major element of the solution, which is reflected in his words, "Coal is an abundant resource in the world ...It is imperative that we figure out a way to use coal as cleanly as possible." However, the public is being led by the media to believe that natural gas is the salvation for reducing Greenhouse Gas (CHG) emissions from coal.

The war has just begun over the proposed maximum achievable control technology (MACT) environmental requirements, Greenhouse gas rules, and other new emission focused EPA regulations that will drive the power utility industry to make very costly modifications to their large power plants, while struggling over to replace or mothball smaller less cost effective plants. The options for the future come down to the transition to an uncertain world of natural gas, or construction/retrofit of coal plants that are capable of carbon capture and storage (CCS). Without clear economic drivers (e.g., cap and trade) to justify conversion to CCS capable plants, the Department of Energy (DOE) has had to step up and offer alternatives. They are sponsoring a number of projects to evaluate the options for CCS on Integrated Gasification Combined Cycle (IGCC) and Oxy-coal Combustion (OCC) plants.

This paper reflects Air Liquide's efforts in improving the viability of clean coal production with development of highly efficient oxygen generation, CO₂ management and other related capture technologies. Advanced power plants of today (IGCC or OCC) are environmentally enhanced by the elimination of air for combustion in favor of oxygen, which significantly reduces contaminants in the syngas stream. Air Liquide, the world's leader in industrial and medical gases for over 100 years, continues to invest in the improvements for cryogenic air separation unit (ASU) and a new concept for Oxy-Combustion plants, a CO₂ Cryogenic Compression and Purification Unit (CPU). Over the past 30 years, Air Liquide has made great strides in advancing the design of ASUs to improve the efficiency of large industrial plants and reduce cost

through better integration and enhancements in the ASU design. Through optimization of the CPU, a greater than 20% reduction in the parasitic load required for the ASU (when compared to the world's most efficient ASU) has been achieved and even better results (i.e., ~30%) are projected by 2015.

Air Liquide's innovative CO₂ CPU was specifically developed to purify and capture CO₂ from fossil power plants. The CPU is tailored for specific plant configurations and includes removal equipment for several impurities along with low pressure impurity treatment, compression, partial condensation and distillation to produce a high purity CO₂ with near zero emissions. Significant development work over the last ten years has been required to optimize the CPU and adapt it as a capture technology focused on flue gas conditions and emissions specifications to be able to meet the EPA MACT and other new emissions related regulations. Several CPU designs have been tested at increasing larger scales from bench to a commercial plant. The progression of both the ASU and CPU technologies will be described in this paper.

Mid-2010, the DOE announced the next major step in Oxy-Combustion by the award of \$1 billion to Ameren Energy Resources (AER) and its partners Air Liquide and B&W, and the FutureGen Alliance (FGA) to build FutureGen 2.0. The project will repower the Unit 4 at Ameren's Meredosia Plant, which includes a 200 MWe super critical steam turbine, with an oxy-combustion system that includes CCS. Air Liquide Process & Construction will provide the ASU and CPU, B&W will provide the Oxy-fired boiler and gas quality control system. Ameren, the plant owner, will provide project management and balance of the plant responsibilities. The FGA will be responsible for the transportation, wells, storage and monitoring of about 3,300 tpd CO₂ from this AER clean coal facility. The current status of the FutureGen 2.0 Project will also be discussed in this paper.

FutureGen 2.0 CO₂ Pipeline and Storage Site Project Steve Winberg, CONSOL Energy Inc., USA

FutureGen 2.0 is a first-of-its-kind, near-zero emissions coal-fueled power plant. In cooperation with the U.S. Department of Energy (DOE), the FutureGen 2.0 project partners will repower Ameren Corporation's power plant in Meredosia, IL with oxy-combustion technology, will capture approximately 1.3 million tonnes of CO₂ each year and store the CO₂ in a deep saline formation, known as the Mount Simon formation. The project plans to capture and sequester more than 90 percent of the plant's carbon emissions. Other emissions will be reduced to near-zero levels. Ameren Corporation has responsibility for repowering the Meredosia plant, along with Babcock and Wilcox and Air Liquide, using oxy-combustion technology. The FutureGen Industrial Alliance has responsibility for siting and building the CO₂ pipeline and storage site. Members of the Alliance include some of the largest coal producers, coal users, and coal equipment suppliers in the world. This presentation will provide a historical review of the project, a summary of CO₂ pipeline and sequestration siting activities to-date and a review of the project moving forward. The oxy-combustion and CO₂ capture aspects of FutureGen 2.0 will also be covered in this session, with separate but complementary presentations given by Babcock & Wilcox and Air Liquide.

ITEA-ENEL Isotherm Flameless Pressurized Oxy-Combustion for Coal Fired Zero Emission Plant: Recent Results and Technology Development Update

Massimo Malavasi, ITEA S.p.A.; Nicola Rossi, ENEL S.p.A., ITALY

Flameless Pressurized Oxy-combustion is a very recent, and yet promising, fast growing player among the "Near zero" emission coal-fired power technologies scenario.

The "5 MWth" four year development phase ended up in 2010, scoring upsides in all key theoretical basic performances originally projected for experimental confirmation. Ease in the coal water-slurry pumping, all-in-one in the combustor six-nine conversion and zero carbon molten slag segregation from fumes, limited residual ashes and SO₃ down to 1-2 ppm in exhaust gas, these are the performances worth of mention among the numerous positives.

The detailed engineering design of a 50 MWth Isotherm coal pilot unit, incorporating a brand new USC velox boiler also, it is almost completed.

The demonstrated features of Isotherm represent a leap vs traditional, and CCS competing technologies. The novelties are such to suggest ENEL to initiate, in parallel to the pilot, the FEED of a 350 MWe demonstration unit, so that to ground as soon as possible with engineering design all potential capex savings and running cost reduction provided by the simple, short train, high efficiency unit operations, of Isotherm technology.

Flameless pressurized Oxy-combustion has been pioneered and patented by ITEA Spa, Italian company of the Sofinter Group. The development and exploitation for coal fired power production is performed in cooperation with ENEL Spa, utility co-leader in Europe.

Technology achievement, and ongoing developments steps are reviewed.

SESSION 38 **Gasification: Fundamentals**

Mineralogical Analysis of Coal Chars Obtained by High Temperature Gasification of Gravity and Size Separated Fractions of a High Volatile Bituminous Coal

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Coal is a heterogeneous mixture of organic matter and inorganic minerals, but the mineral distribution can vastly vary within a seam. During the grinding of coal for entrained flow gasification, some minerals (excluded minerals) separate from the macerals, but others remain closely associated to the organic matter (included minerals). Gravity separation of the feedstock enables us to study the heterogeneous nature in separate particle classes. These coal particles, depending on their mineral associations, behave differently when fed into a gasifier in terms of carbon conversion, mineral transformations and time-temperature history. In order to predict and quantify flyash formation as well as carbon conversion during gasification, a thorough understanding of the mineral transformations in the coal particles is required.

The simplest method (a destructive technique) to determine the constituents of original minerals is by determining the major and minor oxides by atomic emission spectroscopy (AES). Computer controlled scanning electron microscopy (CCSEM) is deployed to measure the mineral composition based on Energy Dispersive Spectroscopy (EDX). CCSEM is also used to classify the nature of the minerals whether present as included or excluded. The technique provides accurate information without transforming the samples chemically, but physically the samples are sealed into resins. Quantitative mineralogical analysis by X-Ray diffraction (Rietveld method) is an attractive method to non-destructively measure the mineral phase compositions. ICP-AES is well suited to large scale batch runs, but information on mineral transformations is lost. In this paper, we compare certain analytical techniques used in the mineralogical analysis of gasification chars obtained in a drop tube reactor and follow the chemical path of the minerals in the original coal samples during the gasification process.

The coal was separated into four gravity fractions by float-sink methods and each gravity fraction was sieved into seven particle fractions. Strong presence of iron and sulfur was measured by ICP-AES and ASTM sulfur analysis in all the heavier particle classes. In particular, the iron and sulfur content were at elevated levels in the finer particle classes in three of the gravity fractions. Silicon, aluminum and calcium were also measured in the ash from the heavier fractions. Both XRD and CCSEM techniques were used to measure the major minerals of pyrite, quartz (silica), kaolinite, illite and gypsum in the coal and the gasified chars. The measured values were within acceptable ranges from both techniques and the iron mineral content was additionally corroborated by Mossbauer spectroscopy. Experimental data obtained showed the usefulness of XRD for quantification as a fast and accurate method for measuring pyrite and kaolinite in the coal and the coal chars. It was observed that the XRD technique tends to over predict quartz content and under predict pyrite content when compared to data from the CCSEM.

Particle Deposition Predictions by Critical Viscosity and Mechanistic Particle Deposition Models

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The mechanistic ash particle deposition model of Ai [1], based on JKR theory [2] and work by Brach and Dunn [3] and Soltani and Ahmadl [4], and a critical viscosity-based deposition model proposed by Walsh *et al.* [5], using the viscosity relation of Browning *et al.* [6], have each been used to predict the ash particle deposition behavior measured experimentally by Ichikawa *et al.* [7] in an ash heating tube that was designed to simulate ash temperature histories in a gasifier. Their particle impact surface was cooled to representative temperatures of syngas convective cooler heat exchanger tubes. Experimental ash heating temperatures ranged from 1573K to 1873K, spanning the ash melting temperature. FLUENT DPM CFD numerical simulations of the Ichikawa *et al.* experiments were used to predict ash particle trajectories and particle impact velocities and impact temperatures, which were then used as inputs into the two particle deposition models. The CFD simulations used the realizable $k-\epsilon$ turbulence model to compute the gas flow field and the heat transfer to the steel particle impact probe, and DPM particle tracking for the particle trajectories and temperatures. The predictions for the mechanistic deposition model [1] have recently been documented by Ai and Kuhlman [8].

For the mechanistic particle deposition model [1], the frequency histogram comparisons of adhesion and rebound behavior by particle size showed good agreement between model and experiments for each of the four ash heating temperatures. However, the critical viscosity model gave predictions that were both inaccurate quantitatively, as well as predicting the wrong trends for deposition versus particle diameter at each ash heating temperature. Specifically, first, while both models correctly predicted the trend of enhanced overall particle mass deposition as the ash heating temperature was increased, the mechanistic deposition model captured this

quantitative change more accurately than the critical viscosity model. Further, the critical viscosity model predicted increasing deposition for the larger diameter ash particles at a fixed ash heating temperature, since they tended to have higher temperatures upon particle impact, while both the experimental results and the predictions of the mechanistic deposition model had lower particle deposition efficiencies for the larger particles. The present work shows a limitation for deposition models based upon a critical viscosity concept when the ash particles experience a rapid cooling, as in the Ichikawa *et al.* experiments.

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Coal Ash Behavior in Reducing Environments (CABRE) III

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A follow-on program to previous ash behavior studies has been initiated at the Energy & Environmental Research Center (EERC) at the University of North Dakota. This program is cofunded by the U.S. Department of Energy through the EERC's National Center for Hydrogen Technology® (NCHT®) and a consortium of industrial sponsors. The Coal Ash Behavior in Reducing Environments (CABRE) III Program is focused on developing models that accurately predict the fate and transformation of inorganic material from coal and petroleum coke in reducing environments. The goal of the program is to provide a computer model that will enable commercial gasification facilities to be able to predict and control ash deposition in all areas of a gasification system. Specific areas of interest include elemental transformation and ash viscosity predictions. The EERC is using laboratory-scale measurements in conjunction with small pilot-scale gasifier runs to determine and ultimately predict the partitioning of ash components in a gasification system. A small pilot-scale entrained-flow gasifier and a fluid-bed gasifier have been used to develop the data on sponsor fuels.

The program is occurring over three phases: I) development of fundamental laboratory data on sponsor fuels, II) gasification testing of sponsor fuels and data collection, and III) data incorporation and model development and validation. Phases I and II of the project have been completed, and the draft version of the working model is scheduled to be ready in the fall of 2011. This paper reviews the current progress of the program and discusses the results of the gasification test runs.

Toward a Technology to Mitigate Syngas Cooler Fouling

Mike Bockelie, Kevin Davis, Adel Sarofim, Reaction Engineering International; Kevin Whitty, Ignacio Precadio, University of Utah, USA

Coal gasification plants have exhibited sub-par performance and plant economics due to poor reliability and availability. A major contributor to the poor performance has been fouling of the syngas cooler located downstream of the gasifier. The fouling is due to vaporized ash from the coal gasification process depositing on the fireside surface of the tubes in the fire tube heat exchanger used for convective syngas cooling. At present the understanding of the fouling mechanism for coal gasification is not adequately understood for equipment vendors to develop an effective solution. Through funding from a DOE SBIR Phase I project, Reaction Engineering International (REI) has investigated deposit formation in the syngas cooler and soot blowing techniques to remove the deposits from heat exchanger surfaces. In this paper we will provide an overview of small experiments performed at the University of Utah and modeling performed by REI. Example results for deposit formation and removal will be described.

Multi-Scale Approach to Validate Ash Fate Models in Entrained-Flow Slagging Gasifiers

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The reliability and performance of entrained-flow gasifiers depends heavily on the fate of ash. Many qualitative indices have been devised to quickly and easily predict ash slagging/fouling in combustion and gasification systems. However, these indices do not account for the multiple chemical and physical phenomena ash incurs. As a result, they may provide misleading results and are often limited to specific fuels and reactor designs. To obtain reliable quantitative predictions for ash transformations and interactions within a gasifier, various ash phenomena must be studied in detail with models describing each. Models available in literature are reviewed and potential weaknesses are discussed. These models cover ash particle formation, gas-particle transport, particle sticking, slag flow and slag-refractory interaction. Data and correlations for ash and slag properties are also presented. Since most ash phenomena models lack substantial validation data, a multi-scale study has been undertaken to investigate the fate of ash in entrained-flow gasification systems. Select fuels have been characterized by CCSEM and their particle size distributions were obtained by laser diffraction. Slag viscosity measurements were performed with their expected slag compositions. These coals were fed to a 1 ton/day pilot scale gasifier which allowed in-run temperature readings, gas sampling and fly ash sampling. Post-run slag and refractory samples were analyzed. Data collected is crucial for the validation of ash fate models and comprehensive gasifier CFD models.

SESSION 39

Gasification: General – 2

Development of Novel Spinel Refractories for Use in Coal Gasification Environments

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Work has been performed by Oak Ridge National Laboratory (ORNL), in collaboration with an industrial refractory manufacturer (Minteq International, Inc.), an academic research partner (Missouri University of Science and Technology) and end users to employ novel refractory systems and techniques to reduce energy consumption of refractory lined vessels found in industries such as aluminum, chemical, glass, and pulp and paper. The objective of the project was to address the need for new innovative refractory compositions by developing a family of novel MgO-Al₂O₃ spinel structured unshaped refractory compositions (castables, gunnables, shotcretes, etc) utilizing new aggregate materials, bond systems, protective coatings, and phase formation techniques. As part of the four-year project funded by the U.S. Department of Energy (DOE), materials have been developed specifically for coal gasification environments. Additionally, work has been performed to develop and apply low cost coatings using a colloidal approach for protection against corrosion attack of the refractory brick and to develop a light-weight back-up refractory system to help offset the high thermal conductivity inherent in spinel materials. This paper discusses the development of these materials, along with preliminary results achieved toward the reduction of chemical reactions and mechanical degradation by the service environment.

Evaluation of Viscosity Models for Slagging Entrained Gasifiers Using Bituminous Coals

Thiago Fernandes de Aquino, Brazilian Coal Association - SATC/DOE/NETL, BRAZIL; LaTosha Gibson, The Pennsylvania State University/DOE/NETL; John Kuhlman, West Virginia University/DOE/NETL; Esmail R. Monazam, James Spenik, Lawrence J. Shadle, DOE/NETL, USA

NETL has developed a CFD model to simulate entrained-flow coal gasifiers of individual coal size and density fractions which exhibit distinctive fluid dynamic and slagging behavior. The relevant gasification and mineral transformation data for those subsets have been obtained. One approach to evaluate the slagging behavior of these various fractions is to characterize the viscosity of the char minerals and relate that viscosity to critical viscosity measurements. To that end several available viscosity models were tested by comparing with viscosity data available in the literature. A Pittsburgh No. 8 coal was fractionated by both size and density. These size and density cuts were then characterized including the composition of the high temperature ash. The models have been applied considering the different mineral content of those size and density fractions. Models tested included those developed by Urbain, Kalmanovitch (modified Urbain), Browning, and S² correlation used in studies done by Seggiani. These expressions are based on the composition of the high temperature ash such as the acid to base ratio. The temperature of critical viscosity was evaluated to determine the transition from Newtonian to non-Newtonian behavior. One drawback of these models is that they were developed for slags typical of metallurgical processes

and not for slags typical of coal gasifier chars. Relevant viscosity data from the literature was compared against each model. The goal was to select the model which best represented the thermo-mechanical behavior of this coal under gasification conditions. According to the models the highest specific gravity with the most iron content had the lowest viscosity over the entire temperature range of interest. For each density fraction, there was very little influence on viscosity from the changes in ash composition typical for those found in different particle size fractions. The influence of factors found to be important in these viscosity models will be reviewed. The limitations and constraints of each model will be discussed. In the present work, the viscosity models will be incorporated into the gasifier particle population and the impact will be tested on the relative split of slag and flyash produced for the specified coal feed. Variations in the coal preparation procedure to alter the size and density cuts will be indicated.

Temperature Measurements in an Entrained-Flow, Slagging, Coal Gasifier Using Laser Absorption of Water Vapor

Jay B. Jeffries, Kai Sun, Rito Sur, Ronald K. Hanson, Xing Chao, Stanford University; Randy J. Pummill, David A. Wagner, Kevin J. Whitty, University of Utah; Robert C. Steele, Electric Power Research Institute, USA

The design, validation, and demonstration of a sensor for gas temperature using tunable diode laser absorption of water vapor was investigated for a pilot-scale, entrained-flow, oxygen-blown, slagging, coal gasifier. Gas temperature was determined by the ratio of absorption on two water vapor transitions near 1.4 μm with different internal energy. Lasers and electronics were remotely located in the gasifier control room and laser light was directed to the measurement locations in the gasifier using optical fibers. At pressures up to fourteen atm (200 psig), three different measurement locations in the gasifier were investigated: (1) in the core of the reactor, (2) at the exit of the reactor where a water spray quenches reaction chemistry (prequench), (3) in the gasifier product stream before particulate clean-up (post-quench). This measurement environment presents significant challenges to laser-based diagnostics as the absorption transitions in the target molecular species are broadened by the elevated gasifier pressure, transmitted laser light through the synthesis gas is severely attenuated by particulate scattering, and molten slag can block the optical access in the reactor core. Successful measurements were conducted in all three measurement locations, although measurements in the reactor core were limited to measurement times free of slag blockage of the optical port. The laser extinction from particulate scattering ranges from a few percent at some conditions to more than 99.9% at others. Stanford's novel, power-normalized, wavelength-modulation strategy showed good promise for quantitative measurements even with quite large non-absorption losses in the transmitted laser power. Proof-of-concept measurements for CO, CO₂ and CH₄ were performed in the syngas flow at the post-quench location. Quantitative measurements of these species and H₂O offer prospects for a monitor of the syngas heating value.

Impact of Coal-Derived Impurities on the Performance of Hydrogen Separation Membranes

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In order to facilitate the use of hydrogen in integrated gasification combined-cycle (IGCC) applications or as a transportation fuel, hydrogen-from-coal technologies that are capable of managing carbon will be needed. Many technologies are under development for the separation of hydrogen from coal-derived syngas, and among the most promising are hydrogen separation membranes. Studies indicate a significant IGCC plant efficiency increase can be realized if warm-gas cleanup and hydrogen separation membranes are used in the place of conventional technologies. These membranes provide the potential to produce hydrogen while simultaneously separating CO₂ at system pressure. Membrane development to date has primarily occurred on bottle-derived syngas, and the impact of coal-derived impurities is unknown. Gasification syngas typically has many impurities that, if not removed, will poison most hydrogen separation materials. In order to commercialize this promising technology, scale-up to bench- and pilot-scale gasifiers is required so that the impact of impurities can be evaluated.

The Energy & Environmental Research Center (EERC), together with the U.S. Department of Energy's National Energy Technology Laboratory and the State of Wyoming, has developed a project to evaluate the performance of hydrogen separation membranes on coal-derived syngas. EERC small pilot-scale gasifiers were used to produce the syngas, and solid sorbents were used for warm-gas cleanup and water-gas shift. Three hydrogen separation membranes were exposed to coal-derived syngas for hundreds of hours. This paper presents the results of the warm-gas cleanup and membrane tests and provides insights into the potential economic advantages of hydrogen separation membranes over conventional low-temperature technologies.

SESSION 40

Carbon Management: CCS and GHG Abatement – 2

Integration of Rankine and Brayton Cycles Reduces Penalty Due to Post-Combustion CO₂ Capture

Enad Sarunac, Carlos E. Romero, Lehigh University; Barry Liebowitz, New York State Energy Research and Development Authority, USA

Coal-fired utility boilers generate over 50% of the electricity in the United States. Concerns about the effect of anthropogenic emissions of carbon dioxide (CO₂) on global climate will undoubtedly result in regulations restricting CO₂ emissions from existing and newly built emitting sources. While the oxy-fuel, IGCC, and post-combustion carbon capture and sequestration (CCS) technologies are viable options for the new power plants, it is likely that significant percentage of the existing power plants will be retrofitted with post-combustion CO₂ capture technology. The major barriers to implementation of this technology are high cost, significant reduction in power plant output, and high performance penalty.

This paper presents results of the project funded by NYSERDA under PON 1193 concerning efficiency (heat rate) improvements that can be achieved at existing power plants by thermal integration of the Rankine and Brayton cycles, reboiler, and CO₂ compression train using heat recovered from the Brayton cycle hot exhaust, boiler flue gas and the CO₂ compression process to increase steam flow through the steam turbine and reduce low pressure (LP) turbine steam extraction for the mono-ethanol amine (MEA) regeneration in the CO₂ scrubber.

Two options were considered for the Brayton cycle: hydrogen- and syngas-fired turbine. In the later case, syngas is produced by gasifying biomass. Leftover char is burned in the boiler. As a result, there are no CO₂ emissions from the Brayton cycle, meaning that its power output and heat provided to the Rankine cycle through thermal integration do not contribute to the plant CO₂ footprint.

Several heat integration options were analyzed. The results are presented and compared to conventional integration of the MEA CO₂ capture with the steam turbine cycle. The analysis was performed over a range of reboiler specific heat duty from 2,350 to 1,200 Btu/lb CO₂ (5.47 to 2.79 GJ/tonne CO₂) to address the effect of improved and advanced amines on plant performance and capacity.

Current and Future Technologies for Power Generation with Post-Combustion Carbon Capture

Robert W. Stevens, Jr., DOE/NETL, USA

The U.S. Department of Energy's National Energy Technology Laboratory (NETL) is funding research aimed at improving the performance and reducing the cost of conventional pulverized coal (PC) power plants adapted to use post-combustion carbon capture technologies. The objective of this study is to support DOE's Innovations for Existing Plants R&D Program by completing an "R&D Pathway" study for PC power plants that employ post-combustion carbon capture. Eleven post-combustion carbon capture pathway steps have been conceived and assessed that represent a possible scenario for the evolution of the PC power plant technology with post-combustion carbon capture from today's current state-of-the-art systems to future advanced systems. Carbon capture technologies considered in the study include solvent, membrane, and solid sorbent-based systems. The results represent the future potential benefits from successful post-combustion carbon capture technology development. The results also provide a basis to guide technology development and to measure and prioritize the contribution of research and development.

Facilitating CO₂ Capture and Storage for Arizona Coal-Fired Power Plants

Elizabeth Burton, John H. Beyer, Lawrence Berkeley National Laboratory; Robert Trautz, Richard Rhudy, Electric Power Research Institute; Rich Myhre, Bki, USA

Over the last eight years, the West Coast Regional Carbon Sequestration Partnership (WESTCARB) has been investigating and facilitating opportunities for carbon capture and sequestration (CCS) in Arizona through a program that includes geologic characterization, CO₂ source and geologic sink mapping, terrestrial sequestration assessments, power plant retrofit engineering assessments, field pilots, and outreach. The results to date of these efforts will be presented, with a particular focus on the challenges and opportunities of applying geologic sequestration to the large coal-fired power plants in eastern Arizona. Comparisons will also be made to WESTCARB's experiences with CCS in other states and provinces of its region (Alaska, California, Hawaii, Nevada, Oregon, Washington, and British Columbia).

WESTCARB data for industrial and power plant point sources in Arizona show that nine sources emit close to 50 million metric tons of CO₂ per year, whereas in California 33 sources emit nearly the same annual total. This contrast is predominantly the result of differences in the fuel sources and sizes of power plants in each state: Arizona's fleet of large coal-fired plants and California's fleet of relatively smaller natural gas plants. All of Arizona's sources overlie potential geologic storage formations. Furthermore, several of Arizona's large coal plants are located relatively

close to each other, enabling economies of scale and other efficiencies from sharing transport and storage infrastructure. These source characteristics make CCS an attractive option for Arizona to reduce a substantial fraction of its CO₂ emissions.

While the general geology of Arizona is well known, the detailed subsurface data necessary to quantify geologic carbon storage capacity are lacking. These data typically are collected through seismic surveys or drilling done in connection with exploration for hydrocarbons or other mineral resources. Saline formations in the deep sedimentary deposits of the Colorado Plateau in northern Arizona and the intermountain Tertiary basins of southern Arizona account for more than 99 percent of estimated CO₂ sequestration resources in the state but are poorly characterized with respect to the properties of interest for geologic storage. Oil and gas fields, limited to the northeastern corner of the state, account for less than one tenth percent of the state's resource. Coal deposits, while extensive, are too shallow to maintain CO₂ in a supercritical state. The risk associated with the geologic uncertainty of the saline resource is illustrated by WESTCARB's experience in drilling a test well to evaluate the formations beneath the Cholla plant, which emits about 8 million metric tons of CO₂ annually. The target formations were found to have insufficient permeability to support injection of CO₂.

Optimization of Coal-Fired Power Unit Location in Case of CCS

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Traditionally, the power plant location was determined by the fuel and water sources, as well as the concentration of electricity consumers. In case of implementation of the carbon capture and storage (CCS) technologies, additional parameters have to be taken into consideration. The most important one seems to be the location of CO₂ storage area or CO₂ utilization process. The capital and operational costs of CO₂ transportation system may impact significantly on the optimal selection of plant location. The idea for its optimization is thus interesting and may be important for decision-making processes taking place in the energy sector.

The main goal of the present paper is to indicate an optimal location of a pulverized-coal (PC) power plant, taking Polish area as domain for potential investments. It is important to mention, that more than 20% of power units in Poland are older than 40 years and 75% are older than 20 years. The erection of new power units is therefore necessary and will take place in the following years. On the other hand it seems, that the only possible way of CO₂ utilization in Poland is storage in depleted gas fields or saline aquifers.

For the optimization process several sets of location data have been formulated. These data deals with the location of sources of fuel and water, as well as, location of the CO₂ storage and electricity consumers. All these places have been identified by geographical coordinates. The decision variables for optimization are coordinates of the newly-build power plant. Two main cases of the power plant configuration have been examined. First is the supercritical PC unit without CCS which is treated as reference case for comparison. The second case is based on the same configuration of boiler and turbine islands as in reference plant, but the plant is equipped in post-combustion CO₂ removal by chemical absorption using monoethanolamine (MEA) and CO₂ compression system. The modified internal rate of return (MIRR) has been selected as an objective function for the optimization. The MIRR is calculated on the system boundary including power plant, coal transportation system, water delivery system, electricity network, CO₂ pipeline and CO₂ storage area. All cost related to mention subsystems have been calculated based on their simulation modeling. The EES software has been used for both system modeling and optimization execution. Genetic algorithm has been used as main optimization tool. Obtained results indicate the optimal location of the coal-fired power unit at fuel source or at CO₂ storage area, depending on unitary costs of transportation of coal and CO₂.

Use of Waste Heat and CO₂ Compression Heat to Reduce Penalty Due to Post-Combustion CO₂ Capture

Nenad Sarunac, Carlos E. Romero, Lehigh University; Barry Liebowitz, New York State Energy Research and Development Authority, USA

Coal-fired utility boilers generate over 50% of the electricity in the United States. Concerns about the effect of anthropogenic emissions of carbon dioxide (CO₂) on global climate will undoubtedly result in regulations restricting CO₂ emissions from existing and newly built emitting sources. While the oxy-fuel, IGCC, and post-combustion carbon capture and sequestration (CCS) technologies are viable options for the new power plants, it is likely that significant percentage of the existing power plants will be retrofitted with post-combustion CO₂ capture technology. The major barriers to implementation of this technology are high cost, significant reduction in power plant output, and high performance penalty.

This paper presents results of the project funded by NYSERDA under PON 1193 concerning efficiency (heat rate) improvements that can be achieved at existing power plants by optimizing performance of the mono-ethanol amine (MEA) CO₂ scrubbing process to minimize reboiler thermal duty, and thermal integration of the reboiler, steam turbine cycle, boiler, and CO₂ compression train using heat recovered from the flue gas and the CO₂ compression process to reduce the amount of steam that needs to be extracted from the low pressure (LP) turbine for MEA regeneration in the CO₂ scrubber.

The regenerative MEA CO₂ scrubbing process was modeled using Aspen Plus. Sensitivity analysis was performed, where parameters known to affect performance of the CO₂ capture process were varied from their baseline level to obtain improvements in the process performance and minimize reboiler thermal duty. The results show that a 26% improvement in reboiler thermal duty can be achieved by optimizing operating process parameters.

The results for a number of analyzed thermal integration options where heat recovered from the flue gas and CO₂ compression heat were used to improve performance of the steam turbine cycle and/or reduce steam extraction for a reboiler are presented and compared to conventional integration of the MEA CO₂ capture with the steam turbine cycle. The analysis was performed over a range of reboiler specific heat duty from 2,350 to 1,200 Btu/lb CO₂ (5.47 to 2.79 GJ/tonne CO₂) to address effect of improved and advanced amines on plant performance and capacity. For this range of boiler thermal duties, thermal integration improves net unit heat rate by 4.8 to 6.8 percent relative to the conventional integration.

The effect of partial CO₂ scrubbing on plant efficiency and capacity was also investigated. Partial scrubbing involves CO₂ capture from less than 100 percent of the flue gas flow and modular design of the CO₂ scrubbing process. Partial CO₂ scrubbing is believed to be first step toward reducing CO₂ emissions from existing power plants which will speed up deployment of the CO₂ capture. Also, depending on how regulations are written, some power generators could opt for early compliance by scrubbing 20 or 30 percent of flue gas and banking CO₂ emission credits. The results show that the effects of partial scrubbing on plant performance are linear.

SESSION 41 Combustion: Combustion Studies – 2

Development and Demonstration of Laser-Induced Breakdown Spectroscopy for In-Situ, On-Line Coal Analysis

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Coal characterization and prediction of slagging behavior has reached great relevance for coal-fired power plant operators; especially, for units subject to large fuel quality variability, fuel switching and coal blending. Laser-Induced Breakdown Spectroscopy (LIBS) and Artificial Neural Networks were used in the development of an on-line system for in-situ coal characterization. The system consists of an excitation Nd:YAG laser, an Echelle spectrometer, a photodiode/amplifier unit, supporting optics and a processing computer, for above-the-coal belt applications. Demonstration of the system was carried out at PPL's Montour Power Station, to measure elemental composition of the plant coal supply, and the feedstock heating value and ash fusion temperature. A coal inventory composed of a range of twelve bituminous coals, fired at the station, was used to calibrate the system in the laboratory. The results demonstrated the capability of the LIBS technology to detect the following inorganic elements in real time: Al, C, Ca, K, Mg, Na, Fe, S, Si, and Ti. The measurement repeatability for heating value and initial deformation fusion temperature was within ± 76 Btu/lb and 33°F, respectively, for a range of heating values and fusion temperature from approximately 10,500-14,000 Btu/lb and 2,000-2,600°F, respectively. The measurement system is supported by a processing software, which allows real-time display of the coal properties, and will provide expert advice to boiler operators for coordination of coal yard operation, and modification of boiler operation for efficient fuel combustion and mitigation of slagging and fouling.

Pyrolysis and Gasification Reactivity of Brown Coal-Algae Blends

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Combustion and gasification of coal-algae blends have the potential of reducing the carbon footprint from combustion and gasification of coal alone. This paper presents results from an experimental study on pyrolysis and gasification of a Victorian brown coal and a marine algae, first these fuels alone and then as blends of 90:10 to 50:50 by mass. These experiments are conducted in a Thermogravimetric analyzer with steam-injection capability. In general, algae were found to be more reactive than Victorian brown coal during pyrolysis while coal was more reactive than algae during gasification. The reactivity of the coal-algae blends was found to be lower relative to coal alone during steam gasification. But as the pyrolysis and gasification characteristics remains in between the behavior of algae and coal, small percentage of algae can be blended with coal for gasification purposes.

A Petrographic Explanation for Conversion Differences in Two South African Lump Coals
NJ Wagner, N Malumbazo, University of the Witwatersrand,
SOUTH AFRICA

Two high ash, inertinite-rich, medium rank C South African lump coals (-75+5mm) were utilized to study their conversion in a packed-bed reactor combustion unit. Coal A is known to convert more rapidly than Coal B in a commercial operation, despite similar proximate values and vitrinite content. The reactor was run under atmospheric pressure and gases, and attained temperatures of 1250°C. Seven char samples were obtained per coal tested based on the drying, pyrolysis, reduction, combustion and ash bed zones. Chemical structural variations in the char products were determined by proximate and coal char CO₂ reactivity analysis. These analyses were able to reveal that Coal B was less reactive than Coal A, but were not able to provide an explanation as to why. Physical structural variations were determined by FTIR, BET adsorption methods, XRD and ¹³C Solid state NMR analysis. These analyses were able to show that Coal B was more aromatic than Coal A. Detailed petrographic analysis showed that Coal B had a higher reactive maceral content compared to Coal A (54% by volume compared to 35% by volume respectively), as well as a higher total inertinite content (72% by volume relative to 65% by vol.). The reactive maceral content of Coal A was dominated by vitrinite and liptinite (77% by vol.), but for Coal B the reactive macerals were comprised of 49% (by vol.) vitrinite and liptinite and 51% (by vol.) reactive semifusinite and reactive inertodetrinite. Thus it would appear as if this difference in maceral sub-group distribution explains the difference in conversion rate, temperature, degree of aromaticity, surface area. Coal B produced a greater proportion of inert chars and ran at higher temperatures in the hotter region of the reactor. This study demonstrated that the reactivity of lump coals is greatly influenced by the nature of the coal structure and to a lesser extent the kinetics of the conversion process, and the paper highlights the need for a detailed characterization of coals to fully determine their conversion performance; detailed coal petrography is one such tool that's value is frequently underplayed.

SESSION 42
Sustainability and Environment: General – 1

Feeding the Fire: How Coal Technology in Developing Countries May Require More Diversification of Inputs than Initially Argued
Catherine A. McGanity, USA

While nuclear energy was once the long-time rival of coal-based energy systems, the recent natural disasters in Japan strengthened the argument for coal worldwide. However, as developing countries choose coal as the predominant fuel to supply their nascent energy infrastructures, sustainability becomes directly tied to fuel availability and productivity potential, not resource cleanliness. In the highly populated states of China and India, coal availability could prove scarce based upon their respective production and consumption rates (Schnapp, 2010). Furthermore, developing states could find themselves trapped into consuming fuels that are either too expensive to purchase or transport despite earlier predictions of low price ceilings. This has already taken place in states using diesel-based electricity generators (such as SENELEC in Senegal).

Instead of creating systems of dependency on one fuel source, becoming what is known as Input Traps, establishing multi-feedstock methods could ensure energy generation without undermining progress. Adaptation of current coal-based electricity generators to include fuel mixtures, such as coal with biomass, or input switching, such as substituting coal for methane, may also prove useful in developed states. In some cases, input switching can maximize company profits by taking advantage of lower resource prices or minimizing the concentration of greenhouse gases in aggregate annual emissions. Fuel mixtures may also prove exceptionally useful for coal producers excavating seams with high sulfur content or producing high quantities of small, unmarketable coal shards. By minimizing sulfur concentrations and increasing coal shard utility, coal producers could generate higher resale value for their unusable coal as it becomes processed with combustible biomass inputs.

An Example Simulation of Development of Correction Factors for IGCC Power Plant Test Code PTC47.4

Ashok Anand, Michael Gross, M. Mahendhra, Richard Depuy, General Electric Company; Walter Shelton, DOE/NETL; Youssef M Zadeh, Bechtel Power Corp, USA

ASME Performance Test Code 47 (PTC47) was published in 2006 and its associated subsets (PTC47.1, PTC47.2, PTC47.3 and PTC47.4) are being written to provide a frame work for testing and evaluation of integrated gasification combined cycles (IGCC) plants. The paper offers a conceptual approach for IGCC power block performance testing using the proposed Power Block Code PTC 47.4 and discusses the creation of a thermodynamic model of Tampa Electric IGCC power block using commercially available software. Some of the correction curves derived from the

model, which define the performance at design and off design conditions are presented. An example of how the correction curves may be applied is also given.

Economics of Water Capture from Flue Gas using Condensing Heat Exchangers

Harun Bilirgen, Edward K. Levy, Daniel Hazell, Lehigh University, USA

Economic analyses were carried out to determine the costs and benefits of utilizing a heat exchanger system to cool boiler flue gas to temperatures below the water vapor dewpoint. It is assumed the condensed water is treated and then used for cooling tower makeup water and the heat captured from the flue gas is used to preheat boiler feedwater.

Water treatment options for condensed water from flue gas condensing heat exchangers were evaluated, with the goal of using the recovered water in the cooling tower as makeup water. An ion exchange system is recommended for removal of sulfate and nitrate ions and a particulate filtering (suspended solid) system is recommended as the first step in the process. The specific case analyzed is a unit with a wet FGD, where the flue gas leaving the FGD is saturated with water vapor at a temperature of 135°F and with the water vapor volume fraction equal to ~17.5%.

Estimates were made for heat exchanger capital cost and this was converted into an annual fixed charge. The cooling water and flue gas experience pressure drops as they flow through the heat exchanger system and estimates were made of the additional power needed for the ID fan and feedwater pump. In addition, estimates were made of costs of treating the condensate using an ion exchange system.

The benefits include increased turbine power, credit for reduced external water consumption and credit for reduced emissions of mercury and sulfuric, hydrochloric and nitric acids. Analysis of estimated annual costs and benefits shows \$1,277,519 in benefits and \$879,727 in costs. The estimated benefits do not account for any credits due to reduction in mercury or acid emissions.

Groundwater and Ecological Protection for Sustainable Development Under Modern Mining Technologies, Case Study of Shendong Region, West China

J. M. Zhang, D.Z. Gu, Shenhua Group Corporation Limited; Z.W. Shen, China University of Mining & Technology, CHINA

Coal resources, in the next 30 years, will be the main body of energy growth in western China, where the water shortage and the ecological fragility have been major bottlenecks to sustainable development. The modern mining technology will also be tendency for coal mining with high efficiency and high recovery rate. Study focus on the coordinated way to protect the limited water resources from mining damage for sustainable development. Taking the world's largest underground mining area — Shendong area as case, the variation and spatial relationship between groundwater and soil water are discussed, according to characteristics of the large-scale coal mining areas and mining process. Models are proposed regarding three-dimensional structure and groundwater field. Based on practice of study area and model analysis, controlling methods of damage to groundwater and environment were suggested, referring to mining layout, mining face and process optimization, groundwater shift and storage in mined-out area.

SESSION 43
Major CCS Demonstration Projects: General – 5

Carbon Capture Demonstration Project at WA Parish Station Status Update

David J. Stopek, Roger Smith, Sargent & Lundy LLC; John Klumppan, NRG Energy; Satish Reddy, Jeffrey Scherffius, Fluor, USA

NRG Energy has been selected by US DOE to install a 60 MW slip stream CCS demonstration project. The demonstration will be installed at WA Parish Unit 7. The facility will use the Fluor Econamine FG PlusSM technology for the CO₂ capture. Rather than use steam from the existing power plant cycle to provide heat to regenerate the CCS capture solvent, the facility will use a new combustion turbine with a heat recovery boiler (HRB) to provide the thermal energy to the demonstration plant. The design will demonstrate the integration of the CT/HRB including advanced integration concepts that have the potential to provide improved economics for application of CCS technology as a retrofit to existing power plants. CO₂ from the facility will be transported to a nearby oilfield where it will be used for enhanced oil recovery (EOR). This presentation will review the overall design concept of the facility and provide an update on the project schedule. By the time the paper is presented, the facility should have submitted its Environmental Air Permit Application and be well along the way to completion of the NEPA process.

AEP's CCS Activities at Mountaineer Plant - 20MW Demonstration and Future Activities

Gary O. Spitznogle, American Electric Power, USA

In 2009, AEP started operation of the world's first CO₂ capture and sequestration project at a coal-fired power plant. The 20-MWe slipstream capture system is based on Alstom's chilled ammonia process, which captures approximately 100,000 tonnes CO₂ per year and injects the CO₂ into two formations located 1.5 miles below the plant site. With more than 1.5 years of operational experience, the project team has obtained significant information about the capture process, power plant integration details, CO₂ compression, injection strategies, monitoring, and more. This presentation will provide an overview of the project and summary of the findings and results.

The SECARB Anthropogenic Test: The First U.S. Integrated Capture, Transportation and Storage Test

George J. Koperina, Jr., Vello Kuuskraa, David Riestenberg, Advanced Resources International, Inc.; Richard Rhudy, Robert Trautz, Electric Power Research Institute; Jerry Hill, Southern States Energy Board; Richard Esposito, Southern Company, USA

The United States Department of Energy (DOE) seeks to validate the feasibility of injecting, storing and monitoring CO₂ in the Earth's subsurface (geologic storage) as an approach to mitigate atmospheric emissions of CO₂. In an effort to "promote the development of a framework and the infrastructure necessary for the validation and deployment of carbon sequestration technologies," DOE established seven regional carbon sequestration partnerships (RCSPs), representing 40 States, 3 Indian Nations, 4 Canadian Provinces and over 150 organizations. The Southeast Regional Carbon Sequestration Partnership (SECARB), whose lead organization is the Southern States Energy Board (SSEB), represents 13 States within the south eastern United States of America (USA), and includes the core operating area of Southern Company (Alabama, Georgia, Mississippi, and the Florida Panhandle).

In the southeast USA, Advanced Resources International (ARI), in partnership with the SSEB, the Electric Power Research Institute (EPRI), and Southern Company, is participating in the DOE-RCSP Program, representing SECARB. This R&D project (the Anthropogenic Test) is an integral component of a plan by Southern Company, and its subsidiary, Alabama Power, to demonstrate integrated CO₂ capture, transport and storage technology originating at an existing pulverized coal-fired power plant. The capture component of the test takes place at the James M. Barry Electric Generating Plant (Plant Barry) in Bucks, Alabama. The capture facility, equivalent to 25 MW, will utilize post-combustion amine capture technology licensed by Mitsubishi Heavy Industries America. CO₂ emissions captured at the plant will be transported by pipeline for underground storage in a deep, saline geologic formation within the Citronelle Dome, located in Mobile County, Alabama.

Starting in the fourth quarter of 2011, up to 650 tonnes of CO₂ per day will be captured and transported twelve miles by pipeline to the storage site for injection and subsurface storage. These transportation and injection operations will continue for two to three years. Subsurface monitoring will be deployed through 2017 in order to track plume movement in the deep subsurface and to monitor for leakage. This project will be one of the first and the largest fully-integrated commercial prototype coal-fired CCS projects in the USA. This paper will discuss the results to date, including permitting efforts, geologic data collection and analysis as well as detailed reservoir modelling of the storage site, framing the discussion in terms of the overall goals of the project.

SESSION 44 Gasification: Gas Cleanup

Experimental Development of the Sour PSA Process

Jeffrey R. Hufton, Robert Quinn, Timothy C. Golden, Fei Chen, Jeffrey W. Kloosterman, Air Products and Chemicals; Grant Dunham, Michael Swanson, Ann Henderson, Energy and Environmental Research Center, USA

A key challenge for producing clean power or hydrogen via gasification is cost effective purification of the sour syngas. Current purification technology uses a physical solvent absorption process (acid gas removal – AGR) such as Selexol™ or Rectisol® to selectively separate H₂S and CO₂ and yield an enriched H₂ product. High purity H₂ is produced by passing the enriched H₂ through a H₂ pressure swing adsorption (H₂ PSA) system to reject the remaining components. Unfortunately, the AGR processes are expensive and require significant utility consumption during operation, particularly when high levels of CO₂ rejection are required.

Air Products recognized that a H₂ PSA technology adapted to directly handle sour feed gas (Sour PSA) would enable a new and enhanced improvement to a gasification system. If a Sour PSA could be developed to efficiently reject H₂S and CO₂, then it could be directly utilized to produce an enriched H₂ gas turbine fuel in IGCC applications. Higher purity H₂ (99.99+%) for industrial refinery/petrochemical applications could be generated by simply adding appropriate adsorbent layers in the

Sour PSA. A description of efforts to develop this unique separation technology is the focus of this presentation.

Air Products teamed with the Energy & Environmental Research Center (EERC) in Grand Forks, ND, during this project. EERC has extensive experience in generating and handling sour syngas and has become a key testing site for new coal gasification technologies.

The Sour PSA must be capable of handling sour syngas containing CO₂, H₂O, H₂S, carbonyl sulfide (COS), carbon disulfide (CS₂), CH₄, as well as other minor impurities. Our first step was to conduct extended sour syngas exposure tests with multiple adsorbents to identify those that could survive the harsh conditions and maintain adsorption properties. Two adsorbents demonstrated stable operation. Next, a two-bed PSA unit was built and installed next to two EERC gasifiers. In the first set of tests, the PSA was operated with sour syngas generated from sulfur-spiked PRB lignite in a fluidized bed gasifier. A second set of tests was completed with sour syngas derived from Albertan petcoke and an entrained flow gasifier. The latter tests were funded by Alberta Innovates Energy and Environment Solutions. The simple two-bed PSA was able to reject H₂S and most of the CO₂ to the waste stream, producing a H₂-enriched product gas with 1-5 ppm H₂S. Stability of the adsorbent was inferred from periodic H₂S breakthrough experiments. At the end of the tests, the PSA vessels were carefully unloaded and spent adsorbent samples were taken. In parallel with these efforts, the syngas exposure unit was used to determine the impact of select impurities (COS, HF, Fe(CO)₅) on the chosen sour gas adsorbents. The results of these sorbent analyses and tests will be presented.

Crystal Defects and Ionic Diffusion in Calcium Oxide Capture of Acidic Gases from Synthesis Gas and Flue Gas

Zhenchao Sun, Siwei Luo, Liang-Shih Fan, The Ohio State University, USA

Acidic gases present in flue gas and synthesis gas have to be removed from acceptable levels before downstream utilization or direct emission into the atmosphere. Dry removal using solid sorbent has been widely studied because of relatively high process efficiency and some other advantages compared with wet process. Among all the solid sorbents under R&D, CaO-based sorbents attract a lot of attention due to low cost, high availability, and high capture capacity. Previous studies of acidic gas (SO₂, HCl, H₂S, COS, etc) capture using CaO sorbents mainly focus on the kinetics, thermodynamics, and rarely on the ionic transfer mechanism the capture process. Captures of different gases demonstrated inconsistent ionic migration patterns. In SO₂ capture into CaSO₄, the Ca²⁺ cation and O²⁻ anion migrate from the center of CaO solid to the particle surface to form CaSO₄. While in captures of HCl, H₂S, and COS, a counter-current movement of inward diffusion of anion derived from acidic gas and outward diffusion of O²⁻ anion from CaO was found to dominate that ionic transfer process. In this study, these two dominating ionic transfer mechanisms are analyzed and discussed from the diffusion energy barrier and vacancy availability. From these analyses, it can be concluded that loosely-packed crystal structure and high vacancy availability favor ionic diffusivity in solid phase. Extrinsic dopant is suggested to be introduced into CaO crystal structure, which would decrease the compactness of CaO crystal structure and corresponding diffusion barrier.

Pilot-Plant Evaluations for Timely and Cost-Effective Development of Integrated Gasification-Based Processes

Jim Aderhold, Bruce Bryan, Andrew Kramer, Michael Roberts, Gas Technology Institute, USA

Since last discussed at the 24th Annual Pittsburgh Coal Conference in 2007, the Gas Technology Institute (GTI) has expanded its Flex-Fuel Test Facility (FFTF) with the addition of the Morphysorb Acid Gas Removal (AGR) facility in 2008 and the Advanced Gasification Test Facility (AGTF) in 2009. The expanded research facility now comprises a fully integrated pilot-scale research platform to support the development and commercialization of gasification and syngas conditioning technologies as well as integrated process schemes for the production of high value fuels, chemicals, heat and power. It provides GTI, its licensees and industrial partners with a cost-effective means of process evaluation, optimization and risk reduction in the commercialization of emerging end-use applications for syngas. GTI has been involved in the development of gasification and related technologies for over 40 years. Two commercial fluidized bed gasification technologies, U-GAS® for coal or biomass and Carbona/Andritz for biomass have resulted from this work. Current GTI gasification R&D capabilities include feedstock chemical and physical characterization, micro-scale reactivity testing, mini-bench unit (MBU) testing with full-size fuel particles, and large pilot-scale testing from which data is obtained for scaling up to demonstration / commercial units. At the pilot scale, available gasification routes now include air-, enriched air- and oxygen-blown fluidized bed and oxygen-blown, entrained bed slagging platforms at operating pressure up to 400 psig. Gasification fuels supported include biomass, petcoke and all ranks of coal at processing rates up to over 1 ton per hour. Gas cleanup and conditioning options include hot gas filtering, biomass syngas tar reforming, and acid gas (H₂S and CO₂) removal for the full pilot plant syngas stream.

This presentation will discuss recent GTI activities in support of Synthesis Energy System's (SES) commercial deployment of the U-GAS® technology for thermochemical conversion of low quality fuels. It will also review how the

expanded pilot plant facility is being used for testing and development of the Pratt & Whitney Rocketdyne (PWR) compact gasifier and for catalytic tar reforming and conditioning of biomass syngas in support of Carbona/Andritz biomass to liquids (BTL) and renewable natural gas (RNG) projects with UPM and E.ON.

Selectivity Matters

Olaf von Morstein, Johannes Menzel, Uhde GmbH, GERMANY; Dennis Leppin, Gas Technology Institute, USA

The usage of coal gasification is focused more and more on the generation of syngas as a basis for the synthesis of various chemicals such as fertilizers, Fischer-Tropsch products and other synthetic hydrocarbons. The syngas can be used for the production of pure hydrogen as a basic chemical or for hydrogen enriched fuel gas to feed low CO₂ emission IGCC power plants. All these product routes include a partial or a complete CO shift to increase the hydrogen content in the produced syngas.

The Prenflo Direct Quench gasification system and a subsequent sulphur tolerant sour gas CO shift unit provide a cost effective process combination for the production of hydrogen enriched syngas. The water saturated, cooled and pretreated raw syngas from the gasification unit can be directly used as feed gas for the CO conversion process.

However this cost advantage is partially offset by higher investments in the downstream acid gas removal unit (AGR). In this process unit the sulfidic gas components as well as the carbon dioxide, formed by the CO conversion or already present in the raw syngas, have to be separated from the generated product gas. The main challenge is to separate the hydrogen sulphide selectively from the syngas in the presence of a significant amount of CO₂, in order to generate a hydrogen rich acid gas stream for sulphur recovery and a pure CO₂ stream for venting or sequestration.

The design of the AGR unit is largely affected by the selectivity of the applied solvent thus determining the investment and operation cost for this unit. Due to its high acid gas selectivity the Morphosorb solvent offers significant advantages in design of the required AGR unit, reducing complexity, providing savings in investment and operation cost. On the basis of a case study a comparison is made to a second commercially available physical solvent applied to selective acid gas removal from coal gasification derived syngas.

SESSION 45 Gasification: General – 3

Water Shift Modeling in Coal Gasification in an Entrained-flow Gasifier

Xijia Lu, Ting Wang, University of New Orleans, USA

Most of the reaction rates for water-shift process were obtained from experiments under simplified laboratory condition with specific catalysts. Few of the reaction rates without using catalysts were obtained under supercritical condition, with the pressure much higher than those in an operating gasifier. In either case, it is discovered that the published reaction rates are too fast and overpredict the actual water shift rate in a gasifier without the presence of catalyst. This study focus on first discussing the characteristics of water-shift process with and without the presence of catalysts, followed by calibrating the water shift reaction rate to match the experimental data from operating an actual gasifier.

Investigation of the Performance of a Syngas Quench Cooling Design in a Downdraft Entrained Flow Gasifier

Ting Wang, Xijia Lu, University of New Orleans, USA; Heng-Wen Hsu, Cheng-Hsien Shen, Industrial Technology Research Institute, TAIWAN

Syngas coming out of a gasifier is usually very hot. Cooling is necessary to allow syngas to be transported without damaging downstream piping or equipment. Furthermore, the existing cold-stream syngas cleaning technology also requires syngas temperature to be reduced below 600°F. Direct water quenching of syngas is one of the cooling schemes that can provide not only the necessary cooling but also partial water shift reaction to convert steam and carbon monoxide to carbon dioxide and hydrogen, which is an important process for implementing carbon capture and sequestration (CCS). To assist designing an adequate syngas quench cooling section, this study has employed a computational fluid dynamics (CFD) scheme to investigate the performance of a preliminary design of a water quench system in a downdraft entrained flow coal gasifier. The preliminary quench system design consists of a primary water curtain section located in the main entrance of the quench section and a secondary water spray section distributed in the outer annular passage with a counterflow arrangement. The main goal of this study is to use the experimental results to calibrate the CFD model, especially the water-gas shift reaction model. Then, use the calibrated model to help design different water spray strategies to achieve the targeted temperature and syngas composition.

Impact of the Water Quench on the Syngas Composition Obtained from Entrained Flow Gasification of Carbonaceous Fuels

Christian Goersch, Frank Hannemann, Siemens Fuel Gasification Technology GmbH & Co.KG; Thomas Hammer, Siemens AG, Corporate Research and Technologies; Bernd Meyer, TU Bergakademie Freiberg, GERMANY

The Siemens Fuel Gasification (SFG) technology is applicable for a wide range of feedstocks including pet-coke, bituminous coal, lignite and low rank fuels like refinery residuals and biomass. Syngas (carbon monoxide and hydrogen) produced from these fuels can be conditioned, e.g. by catalytic Water Gas Shift Reaction (WGSR) influencing the H₂/CO-ratio, and used for chemical synthesis or IGCC applications. Since during water quench the steam content of the syngas increases while the temperature of the gas mixture decreases, WGSR is expected to convert a fraction of the CO with the steam to H₂ and CO₂. Due to the temperature and concentration profile this effect will be limited kinetically.

Both gas phase with and without slag catalyzed WGSR were investigated by means of thermodynamic equilibrium simulations of gas compositions, numerical simulation considering detailed gas phase chemical kinetics, and experiments performed in a plug flow reactor filled with ground coal gasification slag. Based on the experimental results a single-step catalytic WGSR-model was evaluated.

The results of these investigations show that the H₂/CO-ratio of the syngas obtained from SFG technology increases with higher residence time and quench temperature by gas phase WGSR. Due to the low specific surface area slag catalyzed WGSR can be assumed to play a minor role.

Molten Catalytic Coal Gasification for Methane Rich Syngas

Nicholas Siefert, Carnegie Mellon University /DOE/NETL; Tristan McQuain, West Virginia University/DOE/NETL/ORISE; Jack R. Ferrell III, DOE/NETL/ORISE; Shawn Litster, Carnegie Mellon University; Dushyant Shekhawat, David Berry, DOE/NETL, USA

The U.S. Department of Energy is sponsoring the development of high-temperature fuel cell power systems based on solid oxide technology through the Solid State Energy Conversion Alliance (SECA) program. Recent system studies [1-2] indicate that the system efficiencies of advanced fuel cell power plants can approach 60% while capturing carbon dioxide, minimizing water consumption, and lowering the cost of electricity compared to conventional PC-CCS and IGCC-CCS power plants. One of the keys to achieving this target is the production of a high methane synthesis gas (>20% dry vol. basis) from the gasification of the coal. This enhances the cold gas efficiency of the gasifier and reduces the cooling load within the fuel cell. It is difficult to economically generate a syngas with 20% or greater CH₄ due to a trade-off between kinetics and thermodynamics. While methane can be produced at low temperatures, the kinetic rate of steam gasification of coal is significantly less at lower temperatures. To attempt to overcome this difficulty, the gasification of coal with steam was carried out in a molten bed of alkali cation catalysts at a lower temperature than previous research [3-4].

Parametric studies were conducted to understand the effects of temperature, pressure, catalyst composition and the ratio of coal to catalyst on the performance of the molten catalytic gasifier in terms of kinetics and syngas composition. These runs were performed for both fresh and devolatilized Pittsburgh #8 coal. As expected, the methane composition in the syngas increased with increasing pressure. Also, the kinetics were improved when operating at 2.1 MPa compared with operation at 0.4 MPa. While increasing the temperature of the reactor from 600 °C to 900 °C increased the kinetics of steam-coal gasification, the production-averaged methane composition was not a strong function of the temperature. The largest production-averaged methane composition measured was 18% ± 3% at 800 °C and 2.1 MPa, along with 2.5%±/0.3% of the C₂ hydrocarbons: ethane + ethylene.

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SESSION 46
Carbon Management: CCS and GHG Abatement – 3

Pipeline Environmental Constraints Analysis to Deliver CO₂ From a Coal Gasification Plant

Frank M. Kranik, Gordon Ferguson, Ecology & Environment, Inc., USA

This pipeline environmental constraints analysis evaluates the delivery of CO₂ from a proposed Coal Gasification plant to three possible delivery points in several states for enhanced oil recovery and for sequestration. This power point presentation examines the pipeline corridor review and base route selection process and identifies fatal flaws in pipeline routing that would affect project environmental permitting and provides a general description of key environmental consideration for the pipeline route (i.e. land use, water bodies, wetlands, threatened or endangered species and identifies major permits, agencies and permit requirements and timeframes.

CO₂ Capture at the National Carbon Capture Center

Tony Wu, Ruth Ann Yongue, Southern Company Services, USA

The Power Systems Development Facility (PSDF) is a key national asset for ensuring continued, cost-effective, environmentally acceptable energy production from coal. Sponsored by the U.S. Department of Energy (DOE), the PSDF is an engineering scale test center located in Wilsonville, Alabama. The PSDF staff has effectively developed advanced coal-fired power systems, moving several first-of-a-kind technologies to the commercialization stage. Building on its previous success, the PSDF now houses the National Carbon Capture Center (NCCC), which was established in 2009 to address the nation's need for commercially viable CO₂ capture options for flue gas from pulverized coal power plants and syngas from coal gasification power plants.

The NCCC offers a unique and highly flexible test platform. The site accommodates a wide range of equipment sizes and provides commercially representative flue gas, syngas, and process conditions that allow confident scaling of results to commercial applications, a crucial element in shortening development times. The test facilities consist of two major areas of infrastructure. One is the newly constructed Post-Combustion Carbon Capture Center (PC4), which utilizes a flue gas slipstream from an 880 MW supercritical pulverized coal unit at the adjacent Alabama Power E.C. Gaston Plant. The other is a pilot-scale coal gasification process which provides syngas for testing pre-combustion and related syngas conditioning technologies, such as water-gas shift catalysts.

In collaboration with the DOE and project partners, NCCC engineers have evaluated many post- and pre-combustion processes for potential inclusion in test plans. Several post-combustion technologies were selected for the initial testing in 2011 following the commissioning of the PC4 equipment and baseline solvent testing. Pre-combustion testing has been ongoing for several years, and the facilities continue to support a variety of technology developers. This paper will provide an overview of the NCCC test facilities, the testing completed to date, and future plans.

Analysis of Warm Membrane - and Adsorbent - Based Technologies for CO₂ Capture in IGCC

David J. Couling, Kshitij Prakash, William H. Green, MIT, USA

Electricity generation from coal is a potential method to help address the world's growing energy demands due to coal's relatively large abundance and low cost. Specifically, Integrated Gasification Combined Cycle (IGCC) is emerging as a promising method of coal power generation due to its increased efficiency, especially with regard to the capture of carbon dioxide. Despite these advantages, however, a significant challenge to the large-scale implementation of IGCC is the development of more efficient techniques for pre-combustion CO₂ capture. Previous researchers have directed efforts at increasing this efficiency of separation through the development of membranes or solid adsorbents to capture pollutants at elevated temperatures, often investigating potential materials experimentally. However, not only is this process time-consuming and expensive, but also because these novel techniques have yet to be deployed on a large scale, much is still unknown about their desired operating characteristics.

In this work we present an alternative approach in which potential membrane and adsorbent technologies are evaluated using computational simulations. We model multicomponent gas separation in membranes using both Pd-based composite metallic membranes and polymeric membranes for H₂/CO₂ separations. In addition, we develop a numerical pressure-swing adsorption model to study the chemisorption and regeneration processes for carbon dioxide on solid adsorbent materials. The results of these models are then integrated into an IGCC process simulation within Aspen Plus in order to evaluate optimal operating conditions and corresponding parasitic energy losses of each process. We then use these results to identify the most promising methods for warm CO₂ separation. Finally, we can use the results we obtain to suggest the necessary material properties of the promising membrane and sorbent technologies, potentially providing direction for ongoing experimental work with these materials.

Gas Permeation Carbon Capture – Process Modeling and Optimization

Juan E. Morinelly, David C. Miller, DOE/NETL, USA

A multi-staged gas permeation carbon capture process model was developed in Aspen Custom Modeler® (ACM) and optimized in the context of the retrofit of a 550 MW subcritical pulverized coal (PC) power plant. The gas permeation stages in the process are described by a custom multi-component, hollowfiber membrane model. Gas transport across the asymmetric membrane was modeled according to the solution-diffusion model for the selective skin layer and the assumption of negligible flux resistance by the porous support. Counter-current, one-dimensional plug flow was assumed with permeate pressure drop in the fiber lumen side due to capillary constrained flow. A modular optimization framework was used to minimize the leveled cost of electricity (LCOE) by optimizing a set of key process variables. The framework allows the external control of multiple simulation modules from different software packages from a common interface.

SESSION 47

Carbon Management: CO₂ Geologic Sequestration – Coal

Modeling of Enhanced Coal Bed Methane Recovery and CO₂ Sequestration in Coal Seams

D. N. Saulov, A. Y. Klimenko, V. Rudolph, University of Queensland, AUSTRALIA

In this study, the recently proposed Porous Distance Conditioned Moment Closure (PDCMC) model is used to tackle the problem of modelling of adsorbing, desorbing and reacting flows through coal, which is of a particular importance for such technologies as CO₂ geological sequestration and enhanced recovery of Coal Bed Methane (CBM). The model, which is formulated in terms of singleconditioned expectations, simulates complex processes of convective and diffusive transport of species through a complete cascade of pores of different sizes in a continuous and consistent manner. The model addresses the major difficulty of describing sorption process in porous media with fractal properties, where distant transport occurs in the largest pores or fractures, while the adsorbing or desorbing surface is mainly allocated in small pores.

Experimental measurements of methane replacement by CO₂ conducted at the University of Queensland reveal that, at specific conditions, the decay of CH₄ concentration in the outflow gas follows a power-law, rather than to be exponential. The PDCMC model allows consistent treatment of methane diffusion from smaller to larger pores together with a counterflow of CO₂ induced by the pressure gradient.

As a result, the model can match the power-law observed in the experiments. Ability of the model to simulate different regimes of methane replacement by CO₂ makes it useful for optimizing the operational parameters for such technologies as coal seam CO₂ storage and enhanced CBM recovery.

An Experimental Study to Investigate the Effective Factors for the Performance of Coal Mass Natural Cleat System upon CO₂ Sequestration Process in Deep Coal Seams

M.S.A. Perera, P.G. Ranjith, Monash University; S.K. Choi, CSIRO, AUSTRALIA

Today, numerous researches are started in worldwide to find potential methods to control the carbon dioxide (CO₂), leading greenhouse gas, content in the atmosphere as the excessive amount of it has been severely affected the human life. CO₂ sequestration process in deep un-minable coal seams provides a desirable solution to mitigate the excessive CO₂ content. Coal mass has a natural cleat system, which largely controls the CO₂ movement through it. However, the complex chemical reaction in-between the injecting CO₂ and the coal mass causes the coal matrix to be swelled, which close up the coal mass cleat system, resulting in reduction of CO₂ injection capacity to the coal seam. The main objective of this study is to identify the factors that affect the performance of coal mass cleat system upon CO₂ movement and consequently the CO₂ sequestration process, through an experimental study. The effects of gas injecting pressure, in situ stress (depth) and temperature on CO₂ movement through coal mass are required to and therefore, permeability tests were conducted on 38 mm diameter by 76 mm height naturally fractured black coal specimens using a newly developed high pressure triaxial set-up for CO₂ injection. The effect of injecting CO₂ pressure on coal mass cleat system performance upon CO₂ injection was first examined. According to the experimental results, increasing of injecting pressure causes the cleats performance to be exponentially enhanced. The effect of confining pressure on cleat performance was then examined, performance of coal mass cleat system upon CO₂ movement is significantly reduced with increasing confinement due to the corresponding effective stress increment. From the experimental works on effect of temperature on coal mass, found that, an increase of temperature causes the cleat performance to be enhanced as temperature increment causes the adsorption capacity and the corresponding coal mass swelling to be reduced. And it is also found that Klinkenberg effect to be increased with increasing the CO₂ viscosity. When compared all with all the factors, the gas

injecting pressure is the most significant factor for the cleat performance on CO₂ movement through coal and temperature has the least effect.

An Objective Method to Distinguish Between Adsorption and Dissolution of CO₂ on Wet Coal

Elisa Battistutta, Karl-Heinz Wolf, Hans Bruining, Ali Akbar Eftekhari, Delft University of Technology, THE NETHERLANDS

Gas sorption isotherms have been measured on dry and wet Tupton coal at 318.15 K up to a pressure of 160 bar with the manometric method. The aim of this paper is to determine the relevance of the presence of water for CO₂ sorption on coal. The manometric method requires an accurate equation of state (EoS). Experimental measurements conducted with a density meter show that the density of the CO₂-H₂O mixture in the gas phase can be calculated using the Span and Wagner EoS for pure CO₂ gas. The density of the CO₂-H₂O mixture in the aqueous phase can be described by a Peng-Robinson-Stryjek-Vera EoS optimized for a CO₂-water system. For the interpretation of the coal experiments we also measured the adsorption of CO₂ in a wet unconsolidated sand sample. We show that adsorption experiments follow the computations with the PRSV-EoS. These experiments also allow to determine the partial molar volume of CO₂ in water which agree well with literature data. Given the small amount of water in the coal, adsorption of CO₂ in water only gives a small contribution. Comparison of the dry and wet coal samples shows that the presence of 4.6% of water in the coal reduces the maximum sorption capacity by 16%.

Understanding the Significance of In Situ Coal Properties on CO₂ Sequestration

P.N.K. De Silva, P.G. Ranjith, Monash University, AUSTRALIA

Over the years, the release of carbon dioxide (CO₂) into the atmosphere has increased extensively. There has been an increase of CO₂ concentrations in atmosphere from 280ppm in 1850 to 360ppm in 1998. Therefore, methods such as carbon sequestration, increased conservation or to consume less carbon intensive fuels by switching to alternative energy sources such as wind, solar, nuclear, and tidal power are suggested. However, alternative green energy resources such as solar energy and geothermal energy are not adequate to substitute fossil fuels. Therefore, the dependency on fossil fuels may not reduce in the foreseeable future. The CO₂ sequestration is an attractive method especially in terms of coal with the potential benefits attached with CH₄ recovery. However, the potential of CO₂ sequestration is not understood especially for various types of coals and also due to important in situ properties. In this study, data from previous studies are compared in terms of coal permeability, moisture content, cleat compressibility, ash content and by temperature with the CO₂ adsorption content to understand the significance of these in situ coal properties on CO₂ sequestration.

SESSION 48

Sustainability and Environment: General – 2

Applying Learning Curves to Modeling Future Coal Power Generation Technologies

Ripudaman Malhotra, John Chase, Chris Ordowich, Daniel Steele, SRI International, USA; Michiaki Harada, Keiji Makino, Japan Coal Energy Center (Jcoal), JAPAN

Engineering models based on detailed deconstruction of specific processes are well suited for modeling the efficiency and cost of current plant designs. However, engineering models are not well suited for modeling long-term future technological advancement, which involves significant uncertainty. For example, it is impossible to predict specific parameters of individual performance enhancements such as increases in boiler operating temperature or pressure. Technology learning curves provide a powerful tool for forecasting anticipated performance improvements due to a broad range of technical improvements without specifying the parameters of every possible improvement. Because of the complexity of coal power systems and the number of possible advances or innovations through 2050, SRI chose to use "learning curves" to model the efficiency and cost of power generating technologies through 2050 to build a Coal Technology Futures Model (CTFM).

Coal and natural gas have and will likely continue to be key components of the world energy supply for years to come. Currently, the most efficient commercial technologies for power production are super critical pulverized coal combustion (SCPC), and natural gas combustion with combined cycle (NGCC). Emerging technologies for more efficient power generation from coal include ultra super critical pulverized coal (USCPC), advanced ultra super critical PC, integrated gasification combined cycle (IGCC), integrated gasification fuel cell combined cycle (IGFC), and direct carbon fuel cell. They each have different capital and operating costs leading to different levelized cost of electricity (LCOE). In order to forecast each of these competing technologies under various scenarios of electricity demand, fuel cost, and research investment, we created the CTFM to project the LCOE and efficiency of competing coal power and natural gas technologies through 2050. The model can help planners and policy makers

to see how R&D investments in certain technologies affect the mix of technologies deployed in the future.

We utilized the Analytica® modeling package and included detailed economic calculations to estimate the levelized costs for several types of coal and natural gas power plants with and without carbon capture technologies. Future improvements in plant efficiency and reductions in capital and O&M costs were modeled using technology learning curves that were established by a detailed analysis of historic performance data. We used published estimates of future demand and fuel costs where available, but the model allows the user to easily input other numbers as tables or equations.

The primary output of the CTFM, plant cost and efficiency over time, are driven by learning curves. Adoption of carbon capture was modeled in a variety of ways including being driven by a carbon cap or a carbon tax. The results of the model depict the difficulty of meeting aggressive carbon goals under reasonable assumptions even with the development of new technologies. While there is an extensive literature on the use of learning curves to forecast the cost and efficiency of environmental technologies, we believe this is the first time someone has combined these learning curves with demand projections and a levelized cost method for modeling the adoption of energy technologies.

Acknowledgement. Sponsorship for this project by the Japan Coal Energy Center (JCoal) is gratefully acknowledged.

Techno-Thermal Recycling: A Novel System for Treating Waste Heat as an Energy Resource

Catherine A. McGanity, USA

The second law of thermodynamics dictates the amount of energy created in a system equals the work output of that system; however, work does not constitute of mechanical forces alone. Excess heat created during combustion, also known as waste heat, is also generated and is unpredictably expelled: the transfer of heat created can neither be controlled nor contained to maximum efficiency. While ambient air serves as an ample cold reservoir into which heat can escape, thermal recycling is growing in practice using more dense liquids and nanotech heat collectors to absorb waste heat.

This paper seeks to combine the established technical achievements in the geothermal heat storage community with the various methods for capturing waste heat taking place in coal-based heat engines (and potentially expanding into metallurgical smelting processes as well). Such topics include utilizing liquid-based radiant heat collection and dispersion, long term geo-based heat storage for mass consumption, emerging applications for heat harvesting through nanotechnology, cyclic water utilization for heat recycling, and applicability based on scale.

Integrated BTL Process as Potential Solution for Coal Power Greenhouse Gases

Jacobus Brink, Frans Waanders, Sanette Marx, North-West University, SOUTH AFRICA

Each year millions of tons of greenhouse gases are released during combustion of coal in coal burning power plants. Micro-algal biomass has the potential of capturing these greenhouse gases from coal power plants, with resultant improvements to the environment. Flue gas from coal power plants could be used to grow micro-algal biomass in closed or open-cultivation systems, where microalgae consume the greenhouse gases and assimilate it into their biomass. A new integrated biomass-to-liquids (BTL) conceptual process was developed that could be connected to such a cultivation system to beneficiate the micro-algal biomass into high value fuel, increase the economics of the cultivation system and the overall feasibility of such a greenhouse gas capturing system. The new design incorporates three novel methods for the harvesting of micro-algal biomass, an extraction section to extract oils from the micro-algal biomass, and a biodiesel unit to convert the biomass into high value biodiesel. Biomass rests with a calorific value of 19.27 MJ/kg could be used as a supplement for coal feed to coal-fired power plants, while flue gas from the coal power plants could be fed into the cultivation section, and heat from the flue gas could be used to provide heat for the energy-intensive liquefaction reactor of the extraction section. The new integrated BTL conceptual process has the potential of capturing 26,138 tons of carbon dioxide per year and was designed to process 933,525 tons of wet micro-algal biomass in order to produce 2,228 tons of biodiesel per year from harvested micro-algal biomass.

Environmental and Economic Impacts of Increased Efficiency in Coal Power Plants

Roger H. Bezdek, Robert M. Wendling, Management Information Services, Inc., USA

We find that significant CO₂ emissions could be avoided if the efficiency of existing coal-fired plants is improved and estimate the environmental and economic impacts of engaging in an U.S.-wide efficiency improvement program. This study (funded by the U.S. Department of Energy):

- Discusses the factors affecting the operating efficiency of coal plants
- Identifies feasible efficiency improvements
- Estimates the costs of these improvements

- Estimates the costs and impacts of a widespread coal power plant efficiency improvement (CPPEI) program
- Assesses the impacts of the CPPEI program, including GHGs and jobs
- Discusses broader economic and environmental implications

Efficiency improvements in existing plants are possible from numerous retrofit measures, and such improvements are more cost-effective than building new plants. We estimate that efficiency improvements cost \$25/kW - \$250/kW, whereas EIA estimates the cost of building new coal plants at \$1,800/kW - \$2,800/kW.

The average operating efficiency of U.S. coal plants is 31.8%, and we assessed the costs and implications of increasing this by 15% to 36.8%. We estimated that this would cost \$28 billion -- \$2.8 billion/year, 2010 – 2019. We found that the CPPEI program could result in either expanded electricity generation with no increase in CO₂ emissions or production of the same amount of electricity with significantly reduced CO₂ emissions. In the former case, electricity generation could increase by 225 billion kWh (11%) by 2019. In the latter case, an equivalent amount of electricity could be produced, but CO₂ emissions could be reduced by approximately 250 million metric tons annually and coal production could be reduced by nearly 90 million short tons annually.

Most analyses of the economic and environmental impacts of energy programs focus on the effects of program expenditures. However, our findings indicate that these are overwhelmed by the impact on energy prices, and the implications are discussed.

SESSION 49
Major CCS Demonstration Projects: General – 6

Illinois Basin CCS: Lessons Learned & Future Plans
Scott McDonald, Archer Daniels Midland Company, USA

The Illinois Basin is hosting several major carbon capture and sequestration projects. This basin, which underlies most of the state of Illinois, parts of Kentucky, and Indiana, ranks among one of North America's the best sites for potential storage of anthropogenic CO₂ emissions. Within this basin, the Mount Simon Sandstone, a major regional saline reservoir, is the target for sequestration because it has good permeability and porosity with overlying strata of impermeable shale. Because the regional thickness of this reservoir increases towards the center of the basin, the optimum location for maximum storage of CO₂ is in north central Illinois. Because of the excellent regional geology and access to industrial scale quantities of CO₂, two projects are being conducted at the Archer Daniels Midland Company's (ADM) agricultural processing and biofuel production facility located in Decatur, Illinois. Both projects will demonstrate the ability to inject and store industrial scale quantities CO₂ emissions into the Mount Simon; safely, permanently, and economically for hundreds of years.

One of the projects is the Illinois Basin - Decatur Project (IBDP), announced in 2008, and is lead by the Illinois State Geological Survey (ISGS), through the Midwest Geological Sequestration Consortium (MGSC). This large scale demonstration project will validate the ability of the Mount Simon Sandstone to accept and retain CO₂ emissions. The project, scheduled for start up and operation in the third quarter of 2011, will inject 1.0 million metric tons of CO₂ over a three year period. This project is funded by the U.S. Department of Energy through the National Energy Technology Laboratory via the Regional Carbon Sequestration Partnership Program and by a cost share agreement with the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development through the Illinois Clean Coal Institute.

The Illinois - Industrial Carbon Capture and Sequestration Project (IL-ICCS), announced in June 2010, is lead by ADM and is an industrial scale project designed to sequester and store up to one million metric tons of CO₂ annually. The project, scheduled for startup in the third quarter of 2013 will inject up to 1.0 million metric tons per year over an operational period of approximately 2.5 years. This project is funded by the U.S. Department of Energy through the National Energy Technology Laboratory and by a cost share agreement with the Archer Daniels Midland Company, University of Illinois through the Illinois State Geological Survey, Schlumberger Carbon Services, and Richland Community College.

Both of these projects benefitted greatly from previous work conducted by the DOE's Regional Carbon Sequestration Partnerships (RCSPS). This paper will discuss the lessons learned and future plans for the projects.

One such lesson was learned during the IBDP project. The thorough regional characterization of the Mount Simon was essential in planning and drilling the project's injection well. The well location benefitted from more than two years of regional study which provided the project team with the confidence to drill on the basis of the sites 2D seismic analysis and the regional study. This confidence was shown to be well placed when actual thickness of the Mount Simon was within 50 ft of the estimate even though the nearest well control was more than 30 miles from the site.

The IL-ICCS project has leverage the knowledge and experience gained during the IBDP project. Site selection, reservoir modeling, MVA development, risk assessment, community outreach, engineering design, and facility construction are many of the areas in which the project team benefitted from the experience and lessoned learned

during the IBDP project. Because of this experience, the IL-ICCS project has an accelerated design and construction schedule and plans for operation within 24-30 months.

Port Arthur Project Update: Demonstration of CO₂ Capture & Sequestration for Steam Methane Reforming Process for Large Scale Hydrogen Production, DOE Cooperative Agreement
Number: DE-FE-0002381

Ken Welch, Bob Hutchison, Keith Adams, Kurt Metzler, Kent Kisenbauer,
Air Products and Chemicals Inc., USA

This paper will provide both background and a status update for the Port Arthur, TX project to demonstrate CO₂ capture and sequestration for the steam methane reforming process.

An outline of the topics to be covered is as follows:

- I. Background / summary of the current Port Arthur site and process
- II. Objectives and scope of the demonstration program
- III. Project work / site modifications included in the demonstration program
- IV. Current status of project work
- V. Forward schedule for demonstration period

The Lake Charles CCS Project
Thomas Leib, Leucadia Energy, LLC, USA

The Lake Charles CCS Project is a large-scale industrial carbon capture and sequestration (CCS) project which will demonstrate advanced technologies that capture and sequester carbon dioxide (CO₂) emissions from industrial sources into underground formations. Specifically the Lake Charles CCS Project will accelerate commercialization of large-scale CO₂ storage from industrial sources by leveraging synergy between a proposed petroleum coke to methanol plant (Lake Charles chemical project) and the largest integrated anthropogenic CO₂ capture, transport, and monitored sequestration program in the U.S. Gulf Coast Region. The Lake Charles CCS Project will promote the expansion of Enhanced Oil Recovery (EOR) in the Gulf region and supply greater energy security by expanding domestic energy supplies. The capture, compression, pipeline, and injection infrastructure will continue to sequester CO₂ capture many years after the completion of the term of the DOE agreement.

SESSION 50
Gasification: Underground Coal Gasification

Characterization of the Harmon Lignite for Underground Coal Gasification

Peng Pei, Zhengwen Zeng, Jun He, University of North Dakota, USA

The Harmon lignite bed of the Fort Union Formation (Tertiary Age) beneath western North Dakota presents opportunities for applying underground coal gasification (UCG) technology to recover the unmineable coal resources. However, some characteristics of the formation also present barriers. First, the local aquifers coincide with the lignite bed; second, the lithology of surrounding rocks changes greatly within a short distance. These factors set challenges in site screening, feasibility study and environmental risks assessment. Although extensive investigation work about the Harmon lignite has been conducted, no work was done for UCG application. In this paper, we review the site selection criteria of UCG, and apply the experience and tools of reservoir characterization in petroleum exploration to investigating the structure and properties of a target site in western North Dakota. Information and data from state and federal geological surveys, water resource commission and oil companies are collected. A 3-dimensional model is built to simulate the Harmon lignite bed, surrounding rocks and aquifers. This "coal reservoir characterization" work provides a clear view of the structure and composition of the lignite-bearing formation, as well as a better understanding of its *in situ* geology and hydrogeology. Results of this work greatly facilitate the UCG site selection process. Suitability of the potential site for UCG projects is discussed.

Bloodwood Creek UCG Pilot 2010-2011

Burl E Davis, Cliff Mallett, Carbon Energy Ltd., AUSTRALIA

In October, 2008 Carbon Energy Ltd installed their next generation commercial version of a parallel UCG CRIP module at their site at Bloodwood Creek, 50 km west of Dalby, Queensland Australia. They demonstrated the commercial feasibility of their UCG process at Bloodwood Creek with a 100-day field trial with both air and oxygen/steam injection. The second module, capable of accessing 200,000 tonne of coal during its operational life, is now operational. It will provide UCG syngas to a 5 MW electricity plant, with power being sold into the local electricity grid. The next phase of the program will involve installation of a 25 MW facility for electricity sale into the power grid.

Wildhorse Energy's UCG Technology Provide Clean Independent Energy for Hungary

Johan Brand, Wildhorse Energy Ltd, HUNGARY

Underground Coal Gasification (UCG) provides an exciting opportunity to unlock the energy stored in the coal seams in a sustainable and environmentally friendly manner. The syngas produced from UCG is a flexible fuel which can be cleaned for industrial heating, power generation or further chemical conversion into energy carriers like hydrogen, methanol and substitute natural gas (SNG).

Energy security is also becoming more important because of decreasing production of oil and gas in Europe; coupled with an increasing reliance on imports from Russia; this provides favorable Central European market dynamics as Wildhorse Energy Ltd (WHE) gives the opportunity to these countries to have a domestic supply of clean coal energy.

WHE has several UCG projects with substantial deposits in historic coal mining regions of Hungary, with the main focus on the Mecsek Hills UCG Project. This location has strategic advantages as it is in close proximity to Dalkia (EDF/Veolia) owned Pannon Power Station with established infrastructure. WHE has a MOU with Dalkia Energia for a proposed 20 year gas sales agreement and equity investment.

This presentation shows information regarding WHE and some of the project dynamics and technical solutions and how it may be applicable to this area.

Electrical Resistance Tomography for Monitoring of Underground Coal Gasification

Xianjin Yang, J. Wagoner, A. Ramirez, S. Hunter, R. Mellors, D. Camp, S. J. Friedmann, Lawrence Livermore National Laboratory; Feng Chen, ENN, CHINA

Monitoring of underground coal gasification (UCG) is essential for optimal process control and risk mitigation. We present the use of electrical resistance tomography (ERT) to monitor subsurface cavity growth, which takes advantage of the drastic changes in the electrical resistivity of coal caused by UCG. Electrical resistivity of coal can vary many orders of magnitude from 106 Ohm-m for dry coal to less than 1 Ohm-m for hot (> 650°C) carbonized coal. ERT is a 3D electrical resistivity imaging technique with fully autonomous data acquisition that makes near real-time monitoring possible and affordable. ERT electrodes can be collocated with other downhole tools such as pressure and temperature sensors. Therefore, ERT shows strong potential as an effective and low-cost UCG monitoring tool.

We constructed an electrical resistivity model based on the geology and coal seam parameters of the Wulanchabu UCG project site of ENN, China. A UCG process was simulated in this model and expected ERT measurements were modeled. The synthetic ERT data were inverted to infer the geometry of the UCG cavity and surrounding thermal impact. Both deterministic and stochastic inverse methods provided acceptable images of the cavity geometry, although we prefer the stochastic inversion as it is also capable of integrating disparate data and providing solution uncertainties.

LLNL Release Number: LLNL-CONF-493143.

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Background, Status, and Future of ENN UCG Program

Feng Chen, ENN Sci.& Tech. Co.Ltd., CHINA

ENN Group is committed to the production and application of clean energy, and had set up more than 100 subsidiaries, holding companies and offices in over 80 cities across China and in countries including U.K., USA, Australia, etc. by the end of 2007. According to the characteristics of china coal resource, based on the advanced UCG technology of Russia and United States, in 2006, ENN group collaborated with the China University Mining and Technology (Beijing) and set up the ENN Coal Gasification Mining Co., Ltd to promote the underground coal gasification technology in China. And then, ENN Coal Gasification set up UCG pilot plant in Lang fang (Hebei province) and experiment base in Wulanchabu (Inner Mongolia).

Since October 2007, the ignition is successful, more than 100Ktons of coal has gasified in Wulanchabu UCG field trial site, the heat value of the gas produced from continuous air gasification ranges from 800 to 1200 Kcal/Nm³, while that from continuous oxygen-enrich air gasification ranges from 1800 to 2100Kcal/Nm³. The gas is used to generate electricity, and the power generation has run continuously for more than 22 months. During the past four years, ENN Coal Gasification has made remarkable achievements in UCG technical innovation, for example, introducing the directional drilling technique to construct the underground complex gasifier structure in a short time, and combining high density 3D seismic technology and radon-measurement method to detect the underground combustion zone boundary, meanwhile, ENN Coal Gasification has developed a measuring system for underground temperature field with own Intellectual Property Right. Exploration and attempts were carried out to avoid the UCG process affect the groundwater.

So far, ENN Coal Gasification has built up its own UCG technology system and applied more than 40 patents in UCG field. The Wulanchabu UCG field trial has entered its second phase of commercialization plan to run 200MW power generation, meanwhile, to produce methane 0.5Bm³/y and methanol 0.1Mt/y. the economic analysis of UCG commercialization indicates that compared with surface coal

gasification, UCG technology has remarkable advantages in cost, construction period and payback period after tax.

At present, there are more than 10 UCG projects around the world are running in the phase of commercial demonstration. ENN Coal Gasification has already launched technical licensing with Xiangyuan mining group, GuJiao group, and Zhengzhou coal industry group, these represent ENN Coal Gasification is striving to promote the commercialization of underground coal gasification relying on its mature and flexible business model.

SESSION 51 Gasification: General – 4

Dissipation of Translational Energy During Non-Spherical Particle Wall Collisions as Related to Entrained Coal Gasifiers

LaTosha Gibson, Sarma V. Pisupati, The Pennsylvania State University/DOE/NETL; Balaji Gopalan, Lawrence J. Shadle, DOE/NETL, USA

A fundamental research project has been undertaken by researchers at NETL in the US DOE and Pennsylvania State University to better understand fouling and slagging in coal gasifiers. To predict the partitioning of diverse coal particles into different product streams the aerodynamic behavior and carbon conversion process are tracked and simulated individually. DPM-Eulerian models allow the researcher to track the trajectories of coal and char particles through the gasifier and their impact with the wall. For these computational models, the coefficient of restitution, which is the ratio of the rebound velocity to the impact velocity, is used to characterize particle wall impact behavior. This value is proposed to be used to predict the probability for particle adhesion to the slag layer. Towards that end, cold flow experiments were initially conducted by using an educator to eject high density polyethylene particles onto a flat horizontal steel plate to measure the coefficient of restitution. Meanwhile, high speed video was used to characterize velocity before and after collision with the surface. Based on the results of high polyethylene particles impacting a steel plate, the maximum coefficient of restitution was attained with a rebound angle at 90° while tapering off at higher and lower angles of rebound. Moreover, rotating non-spherical particles were observed in part due to particle-particle interactions and turbulent gas flow eddies. However, the size and sphericity was evaluated as the influence the magnitude of this effect. Such rotational motion can lead to significant energy dissipation upon particle wall collision resulting in a higher damping force in the normal component of motion. To investigate the causes for the wide distribution of the coefficient of restitution values, drop experiments using a vibrating pneumatic feeder were performed to compare the rotational motion determined for both extruded polyethylene and non-spherical coke particles to spherical polystyrene. The coke is a coal derived char produce under slow heating conditions and was used to simulate the behavior and physical properties of coal prior to carbon conversion. Polyethylene is a thermoplastic polymer and was used to simulate the behavior and properties of coal during and after carbon conversion under the thermodynamic conditions of a gasifier. For the most part, the sphericity of char can range from 0.47 (mixed porous type char) to 0.82 (Crassisphere type char) and varies according to the particle size distribution of the original coal. However, the physics, and thus validity of particle wall impact models such as the JKR-Hertz, DMT, and Maugis Models hinges on the geometry of the ideal sphere. The overall objective of this work is to resolve the physics as it relates to the geometry of the particle in order to better adapt the appropriate particle wall impact model to model char and slag interaction in an entrained flow gasifier.

High Pressure Gasification of Coal Under ISO-Thermal Conditions Using Bench Scale HP-TGA

Abhishek Bhargava, Patrick J.Masset, Freiberg University of Mining and Technology, GERMANY

Coal is essentially an important fossil fuel in an integrated gasification combined cycle power plant (IGCC). In this study gasification kinetics of German brown coal were investigated using high pressure thermo-gravimetric analyzer. The main objective was to determine the reaction rate parameters under isothermal conditions (500-1100°C). Initial results show faster conversion rate with the increase in temperatures. However, sudden decline in the rate of weight loss is observed at higher temperatures indicating a probable change in the reaction mechanism. Several models were retrieved from the literature to calculate the Arrhenius type parameters. The chosen models account for the various assumptions involved in the transportation of the reacting species to the active carbon sites (mass transport, adsorption, desorption and chemical reaction). We expect to probe the transition of chemical reaction controlled regime at low temperatures to diffusion controlled regime at high temperatures.

Measurement of CO₂ Gasification Rate of Coal Char Under High Temperature and High Pressure for Optimum Design of CO₂ Recycled IGCC

Kouichi Miura, Syunsuke Imai, Mitsunori Makino, Eiji Sasaoka, Ryuichi Ashida, Kyoto University, JAPAN

A mini directly heated reactor (mini-DHR) was constructed to measure the gasification rate handily under high CO₂ pressure of ~2 MPa in the presence of other gases, such as CO and H₂, at $T \sim 1200^\circ\text{C}$. The mini-DHR was made of U-shaped SUS or Pt tubing of 3 mm I.D. The reactor itself was used as a heating element. An electric current of 75 – 150 A and a few volts was introduced to the reactor to heat up the reactor up to 900 to 1200°C. About 1 mg of char was placed in a platinum mesh basket of 1.0 mm I.D. and 10 mm high. The basket with the char sample was placed just above a thermocouple in the reactor. The conversion of char, X , was estimated by weighing the remaining char sample. The X vs. t relationships obtained under various conditions were analyzed to formulate a gasification rate equation based on the Random Pore model in the presence of both CO₂ and CO for a char prepared from an Australian brown coal.

SESSION 52

Carbon Management: CCS and GHG Abatement – 4

Carbon Mineralization via Carbonation of Calcium and Magnesium-Bearing Minerals as Permanent Storage of Anthropogenic CO₂

Greeshma Gadikota, Huangjing Zhao, Peter Kelemen, Ah-Hyung Alissa Park, Columbia University, USA

Carbon mineralization is one of the most stable options for storing anthropogenic CO₂. Mineral carbonation involves reacting minerals containing calcium and magnesium oxides with CO₂ to form their corresponding carbonates which are insoluble in water. This technology can be applied as both in-situ and ex-situ processes. In-situ mineralization entails the injection of CO₂ into Ca and Mg containing geological formations, whereas ex-situ mineralization involves mining of minerals and subsequent industrial processing and carbonation of the dissolved Ca and Mg species into carbonates. The reaction rates would be much faster for the ex-situ cases but the initial cost of in-situ mineralization would be significantly lower. Unfortunately there is not much literature available for the reaction rates of mineral dissolution and carbonation. Therefore, it is very difficult to predict the fate of injected CO₂ in geological formations and how the ex-situ mineralization process should be designed in industrial scale. To answer these questions, this work focuses on determining carbonation rates of silicate minerals such as serpentine (Mg₃Si₂O₅(OH)₄), olivine (Mg₂SiO₄), labradorite ((Ca,Na)(Al,Si)₄O₈) and basalt (mixture of silicate minerals). The availability of these minerals far exceeds the coal reservoir. In the carbon mineralization process, mineral dissolution has been considered to be the rate limiting step. The addition of various chelating agents and chemical additives is known to facilitate mineral dissolution. Thus, this study focuses on the investigation of the effect of various chelating agents such as oxalate, acetate and citrate, as well as other chemical additives including NaCl and NaHCO₃. A differential bed reactor which is designed to capture the fast reaction kinetics during the first few minutes of the dissolution process is used to perform the kinetic and mechanistic studies of mineral dissolution. Importantly, this particular reactor system eliminates the need of a buffer solution for such experimental studies. Suitable chemical additives are selected based on the differential bed experiments. Next, single-step carbon mineralization experiments are performed in a batch reactor for the water-mineral-CO₂ system containing selected chelating agents and/or chemical additives. The reaction temperature (25 – 185 °C) and CO₂ partial pressures (0 - 150 bar) are varied to mimic various geological storage conditions. The extent of mineral dissolution is determined by the liquid analyses of the filtered solution using ICP-AES, while the extent of carbonation and solid composition are studied using the Total Carbon Analysis and X-ray Fluorescence methods. Furthermore, the changes in the morphological structure of the mineral, particle size, porosity and surface area are determined by SEM, Particle Size Analyzer and BET respectively.

Carbon Dioxide Mineralization of Industrial Products

W.K. O'Connor, G.E. Rush, C.A. Verba, DOE/NETL, USA

Carbon dioxide mineralization tests were conducted under a Cooperative Research and Development Agreement (CRADA) with the Ohio Coal Development Office (OCDO). Twenty-two CO₂ mineralization tests were conducted to investigate the CO₂ storage potential of several materials, including coal fly ash and two steel plant product materials, electric arc furnace (EAF) dust, and steel grinding swarf (an iron oxide fume). The test series covered a temperature range from 50-150°C and CO₂ partial pressures (P_{CO2}) from 20-80 atm, using distilled water and bicarbonate carrier solution. Results, based on the chemical and X-ray diffraction (XRD) analysis of the feed and products, indicate that the subject coal fly ashes have limited CO₂ storage potential, while the steel plant materials, particularly the EAF dust, have relatively high CO₂ storage potential. In addition, additional treatment of the grinding swarf may increase

its carbonation potential and/or make iron recovery feasible. The calcium oxide contained in the coal fly ash was found to be bound with sulfur, as anhydrite (CaSO₄), a relatively insoluble compound at the test conditions utilized. Siderite (FeCO₃) was identified by XRD as the primary solid carbonate product from both steel plant materials. While the EAF dust contained a significant concentration (~20 wt pct) of calcium oxide, no calcium carbonate (CaCO₃) compounds were produced until the more aggressive test conditions (80 atm P_{CO2} @ 150°C) were utilized. This was again apparently due to the phase content of the EAF dust, which included a calcium-iron oxide, or ferrite phase, as identified by XRD. The calcium-iron ferrite was apparently insoluble at the lower P_{CO2} and temperatures investigated, as indicated by the lack of any calcium carbonate phases identified in the products from those tests.

Turbomachinery Development for Oxy-Combustion, Coal-Based Power Systems

Rebecca Hollis, Roger Anderson, Keith Pronske, Clean Energy Systems, Inc., USA

Future coal-based power generation systems must utilize de-carbonizing technologies which permit carbon dioxide (CO₂) to be captured and stored. Oxy-combustion of gasified coal (synthesis gas or “syngas”) permits capture and utilization of high quality CO₂. In the oxy-combustion power plant cycle proposed by Clean Energy Systems (CES), syngas and high-quality oxygen provided by an air separation unit (ASU) are combusted to form a working fluid composed primarily of steam and CO₂. CES, in conjunction with Siemens Energy and Florida Turbine Technologies, has been working to develop and demonstrate turbomachinery systems to accommodate the characteristics inherent in oxy-fuel working fluids. The team adopted an aggressive, but economically viable development approach to advance turbine technology towards early product realization. Goals include short-term, incremental advances in power plant efficiency and output while minimizing capital costs and price of electricity. Proof-of-concept testing was completed via a 20MW_{th} oxy-fuel combustor which was used to explore operability and performance limits while operating with a variety of fuels, including natural gas and (simulated) synthesis gas, over a wide range of conditions. The steam/CO₂ working fluid produced by this combustor was used to drive a turbo-generator at CES’ Kimberlina prototype power plant located in Bakersfield, California. Development then began on 1st generation zero-emission power plant (ZEPP) equipment such as a large combustor (170MW_{th}), a modified aero-derivative turbine (GE J79 turbine), and a reheat combustor. Fabrication and preliminary testing of 1st Gen equipment has been completed at CES’ Kimberlina facility.

CES is now in the development stages of its 2nd generation power plant systems where a Siemens SGT-900 gas turbine engine will be modified and utilized in a 200MW_e plant. Like the 1st generation system, the turbine of the SGT-900 will be used as an advanced intermediate pressure turbine and the can-annular combustion system will be modified into a steam reheater to increase plant efficiency. Design studies are being performed into the necessary modifications to adapt the hardware with specific challenges relating to thermal and structural demands of a steam/CO₂ drive gas. Results, challenges, and lessons learned during 1st and 2nd generation oxy-fuel power plant system development are presented here.

Use of Renewable Energy Sources for Fulfilling the Obligations to the European Union

Petr Ruzicka, Jaromír Tauber, Pavel Sedláček, Lubomír Chytka, Brown Coal Research Institute; Tomáš Lorenz, Czech Coal; Peter Fecko, VSB-TU Ostrava, CZECH REPUBLIC

A significant source of energetically useable energy is biomass in which solar energy deposits. The concept of biomass usually means a substance of biological origin as plant biomass cultivated in soil or water, animal biomass, lateral organic products, or organic waste. Theoretically all kinds of biomass can be used for taking energy as the basic building element of a living mass is carbon and its chemical bond contains energy. The plants are considered the fundamental source of biomass because they can create sugars and proteins by solar energy caught in chlorophyll. From the energetic usability point of view, in the Czech Republic it is mostly wood (or sorted waste), straw, and other agricultural remains, and livestock excrements, or energetically useable sorted communal waste or gaseous products created by the operation of sewage water treatment plants.

SESSION 53
Carbon Management: CO₂ Capture – Solvents

Evaluation of Advanced Solvents and Other Competing Technologies for CO₂ Capture from Fossil Fuel-Fired Systems

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The Energy & Environmental Research Center (EERC) is leading the Partnership for CO₂ Capture (PCO₂C), whose focus is demonstrating CO₂ separation and capture technologies at the pilot-scale for fossil fuel-fired systems to help identify the key challenges associated with each technology. The knowledge and data gathered are used to develop strategies for cost-effective implementation of the technologies at the commercial scale. Phase I of the project, now complete, aimed to provide key technical and economic information to examine the feasibility of selected CO₂ capture technologies as a function of fuel type and system configuration. Both postcombustion and oxycombustion technologies were evaluated during Phase I. Oxycombustion results were gathered for four different coal types from the EERC's combustion test facility. For postcombustion capture, performance metrics of several advanced amine-based solvents were compared to those of monoethanolamine (MEA) to determine economic and technical feasibility of each technology. Data from these tests show that for similar test conditions, MEA required 10%–40% more regeneration energy input to achieve 90% CO₂ capture than the advanced amine-based solvents.

Phase II of the PCO₂C Program, which began in September of 2010, aims to further develop promising technologies toward demonstration and commercialization. The focus of the program is the development of lower-cost and more effective capture technologies and their integration into a system that provides substantial economic and environmental benefits. Approximately ten pilot-scale testing campaigns are planned to evaluate several technologies and strategies for implementation. The pilot-scale testing will utilize the existing equipment fabricated during Phase I of the program and/or other systems fabricated for the novel technologies developed during Phase II. The testing will look at eight different technologies, covering three advanced solvents, solid sorbents, an ionic liquid-based solvent, oxy-fired combustion, a slurry-based system, and other advanced equipment. To address the environmental impact of commercially deployed systems, efforts are being made to develop reliable methods for quantifying amine and ammonia slip from the pilot-scale absorber from both MEA and advanced solvents.

The paper to be presented at the 2011 Pittsburgh Coal Conference will focus on the status and preliminary results of Phase II of the project. A review of key Phase I results will also be presented, including economic results comparing postcombustion and oxycombustion technologies.

An Improved SELEXOL™ Processing Scheme that Reduces CO₂ Capture and Compression Costs

Stanislav Milidovich, Raj Palla, UOP LLC (A Honeywell Company), USA

Gasification industry is beginning to adapt stringent CO₂ stream specifications for CCS applications. In a typical gasification designs for segregated H₂S and CO₂ removal into their respective purified streams, the CO₂ produced is at a reasonable pressures but still requires large amount of compression for geologic sequestration or enhanced oil recovery (EOR) applications. The captured CO₂ stream may contain up to five percent of impurities that can be recovered. Some of the components such as CO in the CO₂ stream are currently considered as regulated HAP pollutant. This CO₂ compression has been found to be the single most significant energy sink compared to all other elements in the gasification complex. Meeting the CO₂ purity requirements with conventional systems is cost-prohibitive.

UOP is working on a few innovative schemes that will significantly reduce capture and compression costs and reduce the loss of valuable hydrocarbon components compared to conventional designs. These new processing flow schemes not only reduce the capture and compression costs but also meet the strict CO₂ venting requirements in case of plant upsets. This paper will describes some of the characteristics of the applied flow schemes and provide details on the acid gas removal and CO₂ capture economics.

Role of Double Salt Structure and Formulation on Warm Temperature CO₂ Capture

Prabhakar Singh, Keling Zhang, University of Connecticut; Liyu Li, David L. King, Pacific Northwest National Laboratory, USA

A MgCO₃-Na₂CO₃ double salt was prepared and tested for enhanced CO₂ capture and release in the 300-500C temperature range. The activated MgO-based sorbent compound was synthesized through a wet chemistry technique. Sorbent morphology, chemical composition, and physical properties were examined using standard analytical techniques. CO₂ adsorption characteristics were evaluated using both temperature and pressure swing processes using TGA/DSC technique. Long term performance under dry and moisturized environment was examined in a fix bed

reactor. Commercial MgO was also tested to establish bench mark. Experiments conducted in our laboratory show a capture of 3.4mmol/gr of adsorbent under normal ambient pressure condition. Pressure and thermal swing tests show excellent regenerability and structural stability of the sorbent. A hypothesis for CO₂ adsorption mechanism has been developed and experimentally validated.

Materials synthesis, experimental approach and test results will be presented. Mechanisms for CO₂ adsorption and desorption will be discussed.

Extension of Reversible Carbon Dioxide Binding by Frustrated Lewis Pairs to Other Phosphine and Amine Bases

Robert L. Thompson, URS/DOE/NETL; Sheila W. Hedges, DOE/NETL; Krishnan Damodaran, University of Pittsburgh, USA

Recently, a new approach to metal-free activation of CO₂ using sterically congested Lewis acid/base pairs was discovered which can reversibly bind CO₂ under mild conditions. This reaction was limited to the Lewis base P'Bu₃, which is pyrophoric and difficult to handle in air. A series of alternative Lewis bases, comprised of less-alkaline phosphines and amines, was studied in an attempt to extend the CO₂-complexation reaction to other, more conveniently handled systems. Among the reactions studied, amines tended to form direct acid-base adducts, despite their steric bulk. One system using the amine DBU led to the isolation of crystals which were studied using single crystal X-ray diffraction. None of the alternative Lewis bases studied was capable of complexing CO₂ with B(C₆F₅)₃, presumably due to the diminished basicities compared to P'Bu₃.

The air and vacuum stability of the [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] complex was studied at ambient conditions. A film of [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] was cast from CH₂Cl₂ solution on CaF₂ and stored both in a vacuum chamber for 6 weeks and in the laboratory air for 12 weeks, both at ambient temperature. Neither film exhibited any change over the span of the experiment, suggesting that the bridging-CO₂ complex is remarkably stable and suggests that [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] could be used as a basis for CO₂-capture and storage. Heating the [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] film under vacuum led to the disappearance of the ν(C=O) band at 1694 cm⁻¹ in the FTIR spectrum. Heating the [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] film under vacuum in a sealed system led to free CO₂ with a band at 2349 cm⁻¹ in the FTIR spectrum. TG-MS analyses of [B'Bu₃P-(μ-CO₂)-B(C₆F₅)₃] shows three distinct peaks in the first-derivative weight loss signal beginning at an extrapolated onset of 152°C (maximum dw/dt at 155°C). All three peaks reflect the loss of CO₂ from the compound as determined by the mass spectrum signal at m/z = 44 amu.

Finally, variable temperature ¹³C and ³¹P NMR studies of a mixture of P'Bu₃ and ¹³CO₂ in CD₂Cl₂ were conducted. VT NMR analysis indicates that P'Bu₃ forms an ylide-like adduct with ¹³CO₂ that can be detected and whose relative amount varies with temperature. The results from variable temperature scans permit the estimation of the reaction enthalpy, entropy, free energy, and equilibrium constant for P'Bu₃ and ¹³CO₂. The enthalpy and free energy are small and positive, but the increased solubility of CO₂ at lower temperatures forces the equilibrium towards the CO₂-adduct.

First Principles and Classical Simulations of Ionic Liquids for Carbon Dioxide Capture

Bo Zhang, J. Karl Johnson, University of Pittsburgh/DOE/NETL, USA

Ionic liquids (IL) are promising materials for CO₂ capture due to their thermal and chemical stability. ILs have lower regeneration heat requirements compared with aqueous amine solutions because of their lower CO₂ absorption enthalpy (physical absorption). In addition, ILs have no measurable vapor pressure, and hence will not emit any volatile organic compounds. However, physisorption is not considered to be a viable approach, because the solubility and selectivity of CO₂ in ILs through physical absorption are too low at flue gas conditions. Functionalized ILs capable of specific reactions or interactions with CO₂ are designed to address the issues of solubility and selectivity at low partial pressures of CO₂. We are exploring ILs that can capture CO₂ through chemical interactions. Classical force fields can model the physical interaction between CO₂ and ILs fairly accurately, but they are not typically able to describe the bond breaking/forming events. Therefore, it is necessary to develop a new force field that can properly characterize the chemical interactions. ReaxFF is a very successful formalism for modeling chemical as well as physical interactions with a semi-empirical approach. We are studying the IL [P(C₄)₄][Gly] that has the potential to chemically react with CO₂. Our aim is to develop accurate ReaxFF parameters to allow large-scale simulations of the thermodynamics and transport properties of CO₂/[P(C₄)₄][Gly] mixtures. We use density functional theory (DFT) augmented with the van der Waals (vdW) interactions to explore the chemical and physical interactions between CO₂ and the functional group, [Gly]⁻. Through first principles molecular dynamics, we have found there are different interaction sites for CO₂/[Gly]⁻. One of these can be properly described by chemical binding, while another site could be classified as a quasi-chemical interaction. We also found that vdW interactions are important in determining the binding energies. We obtained several energy profiles along proposed reaction coordinates from our DFT calculations. We have also tested preliminary parameterizations of ReaxFF that are based on similar systems and have tested the validity of the parameterization against our DFT calculations.

Using Novel Phase Change Solvents or High Molecular Weight Silicone Oil for the Pre-Combustion Capture of CO₂

Matthew B. Miller, Robert M. Enick, University of Pittsburgh; David R. Luebke, DOE/NETL, USA

Advanced gasification power plants will employ the water-gas shift reaction producing a high pressure gas-phase mixture containing CO₂, H₂ and water. This gas mixture at elevated pressures provides ample driving force in order to use a physical solvent that will selectively absorb, not chemically bind, to the CO₂. Potential physical absorbers include (a) liquid mixtures of CO₂-philic polydisperse oligomers, (b) small, volatile, liquid CO₂-philic solvents, and (c) CO₂-philic solids capable of melting in the presence of CO₂. The objective of this study was to identify alternative physical solvents that would selectively dissolve only CO₂ from this mixture.

Solid CO₂-philes have been investigated as a potential CO₂ solvent. These solids are typically sugar acetates, or benzene rings having tert-butyl groups and acetate groups attached to the aromatic ring the benzene, or ether oxygens within the ring. The solid solvents that were investigated are β-D-ribofuranose 1,2,3,5-tetraacetate, 2,6-di-tert-butyl-4-methylphenol, 1,2,4-triacetoxybenzene, 2,4-di-tert-butylphenol, sucrose octaacetate, and 1,3,5-trioxane. The unique property of solid solvents is that the CO₂ can be desorbed at an elevated pressure (the three-phase SLV pressure), as opposed to a typical pressure swing desorption pressure that is usually around or a little above 1 atmosphere. The ability of these solvents to melt in the presence of substantial amounts of hydrogen in the gas mixture and selectively absorb CO₂ will be presented. Lastly high molecular weight PDMS has also been investigated at elevated temperatures and compared to poly(ethylene glycol) dimethyl ether, PEGDME. PDMS has shown CO₂-philic behavior in the past and is also completely immiscible with water between 25 °C – 40 °C. Three different molecular weights of PDMS, having viscosities of 10 cSt, 20 cSt, and 50 cSt, have been examined at 80 °C, 100 °C, and 120 °C, respectively. The PDMS was examined in two binary systems first with CO₂ and then with H₂ in an effort to quantify selectivity. If this solvent is capable of operating at these conditions then there would not need to be a cooling step prior to the absorption of CO₂, and water vapor would be able to stay in the fuel gas and be expanded downstream in order to produce power.

SESSION 54

Sustainability and Environment: General – 3

The 3rd Assessment of Pennsylvania's ACT 54 – Protecting Structures, Land and Water Supplies from Underground Coal Mine Subsidence Damages, 2003 to 2008

Anthony Iannacchione, Stephen J. Tonsor, William Harbert, University of Pittsburgh, USA

Laws, governing how environmental impacts from underground bituminous coal mining are anticipated and mitigated, have been evolving within the Commonwealth of Pennsylvania over the last four decades. Initially, with the passage of the Bituminous Mine Subsidence and Land Conservation Act (BMSLCA) of 1966 and the Surface Mining Control and Reclamation Act (SMCRA) of 1977, structures, land, and highways were the focus of action. As time passed, mine operators learned how to mitigate damage to key structures, i.e. homes, garages, barns, silos, etc., and developed methods to fairly compensate property owners. In the mid 1980's new environmental concerns were raised about the BMSLCA. In 1994, the state legislator passed the ACT 54 amendments to the BMSLCA. This law gave coal companies the capability to subsidize the ground using the longwall mining method as long as the potential impacts were identified and planned for during the permitting process and compensation to land owners was provided.

ACT 54 required that these impacts be assessed every five-years. Two previous assessments have been completed; one by the PA DEP and the other by California University of Pennsylvania. The 3rd assessment period, spanning August 21, 2003 to August 20, 2008, was conducted by the University of Pittsburgh, found 456 structures and 108 lands with reported effects occurred from a total 3,735 inventoried structures and 3,587 properties. That is just 12-pct of the total structures and 3-pct of the total properties undermined.

In the early 1980s, interstate highways were first subjected to longwall mining subsidence impacts. During the timeframe of this study, nine longwall panels undermined Interstate 79. The commonwealth spent over 19 million dollars monitoring, maintaining, and repairing the highway. It is estimated that this was a fraction of the cost necessary for the state to condemn the coal and compensate the owners of the mineral rights to prevent longwall mining. Most importantly, no accidents were attributed to longwall mining subsidence and restrictions were limited to reduced speeds and single lane traffic during times of active mining or repairs.

Water supplies became a major focus after the passage of ACT 54. During the 3rd assessment period, 2,789 wells, spring, and ponds were undermined with 683 reported effects accounting for 24.5-pct of the total water supplies undermined. Water supplies

have proven a challenge but they are being resolved. At the end of the 3rd assessment period, 234 reported effects or 34-pct of the cases were still awaiting a final resolution. In late 1990's, the quality and quantity of water flowing in streams undermined by longwall mines became a major focus. The diminution and contamination of streams have been the traditional measures for determining impacts. While the number of stream investigations has varied over the three assessment periods, the amount of technical information collected and kinds of analysis required have changed dramatically. In the early 2000's data became available on the biologic health of streams, largely through the assessment of diversity of the benthic macroinvertebrates (a source of food for fish). In 2005, Technical Guidance Document 563-2000-655 established protocols for assessing biological health and for determining when a stream was impaired and when it attained a resolution of repaired to this reported impact, i.e. low flow or degraded macroinvertebrate diversity. Apparently due to impacts on groundwater flow, resolution of reported flow and biotic quality effects remain a challenge, with approximately half of the reported effects being unresolved at the end of the 3rd assessment period.

The impact to wetlands by undermining continues to elude measurement. The 3rd assessment, examined the Nation Wetlands Inventory database and company documented wetlands from their permit file and from 6-month mining maps, found 93.9 acres undermined. Similar to streams, a new protocol for measuring and characterizing wetlands was introduced in 2005 (Technical Guidance Document 563-2000-655) and implemented in 2007. Recently submitted permit revisions have shown a more significant effort is currently underway by the companies to report accurate wetlands data.

ACT 54 has set standards for the coal mining industry so that environmental impacts are lessened. These standards and the associated protocols are changing and developing as more information and understanding about the impacts is gained and mitigation efforts become more commonplace at coal operations. The 3rd assessment period saw the collection of much more data to more rigorously analyze these impacts. Structures, water supplies, and land features were the early focus of legislation and enforcement. Streams have become a major focus in the last decade, and will likely continue to be, while authorities and industry complete their understanding of the impacts and resolutions. Wetlands are expected to become a major focus going forward.

Projection of Australian Coal Production - Comparisons of Four Models

Mikael Höök, Uppsala University, SWEDEN; Steve Mohr, Geoffrey Evans, The University of Newcastle; Gavid Mudd, University of New South Wales, AUSTRALIA

Coal exports are an important source of revenue for Australia and for this reason Australian coal production and resources have been examined in detail. Two recoverable resource estimates, a Standard case and a High case, were determined. The Standard case calculated the likely recoverable coal resources in Australia to be 317 Gt, whereas the High scenario determined the maximal amount of recoverable coal resources at 367 Gt. The study performed forecasting by use of curve-fitting with Logistic and Gompertz curves as well as Static and Dynamic versions of a supply and demand model based on real world mineral exploitation.

The different modelling approaches were used to project fossil fuel production and the outlooks were compared. Good agreement was found between the Logistic, Static and Dynamic supply and demand models with production peaking in 2119±6 at between 1.9 and 3.3 Gt/y. Contrasting these projections the Gompertz curves peak in 2084±5 at 1–1.1 Gt/y. It was argued that the Logistic, Static and Dynamic models are more likely to produce accurate projections than the Gompertz curve. The production forecast is based on existing technology and constraints and a qualitative discussion is presented on possible influences on future production, namely: export capacity, climate change, overburden management, environmental and social impacts and export market issues.

This paper is based on a study called "Projection of long-term paths for Australian coal production - comparisons of four models" earlier published in International Journal of Coal Geology, Volume 86, Issue 4, June 2011, Pages 329-341

EPA Mandatory Reporting Rule and PSD BACT: Effects on Coal, ECBM and Lessons Learned from the First Year of Implementation

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The fossil fuel industry (e.g. coal, CBM, electric production) is under an ever changing, ever increasing ever tightening regulatory climate that requires consideration of Best Available Control Technologies (BACT) for any new or modified Prevention of Significant Deterioration (PSD), Title V or EPA's Mandatory Reporting Rule (MRR) requirements. In principle, Carbon Capture & Storage (CCS) would provide reduction of greenhouse gases and therefore should be considered. However, since CCS is neither a proven commercial technology nor is it mandated (as of yet), it seems that requiring consideration now is confusing at best. The EPA has enacted strict compliance requirements for the Mandatory Greenhouse Gas Reporting Rule (MRR) that encompass the CCS industry, coal and natural gas production – all of which impact coal!

EPA guidance states that permit applicants and permitting authorities should consider all "available" GHG control options that have the potential for practical application to the source under consideration. The guidance further suggests that once permitting

authorities gain experience with GHG BACT determinations, useful information on GHG permitting decisions will be presented. The expression of regulatory decisions and permitting based on “future tense” terms makes planning, operational and strategic decisions very difficult for the electric generation market. This presentation will endeavor to discuss and navigate specific details and lessons learned from the first year of the PSD and MRR requirements for coal mining, natural gas production (CBM) and power generation as they apply to carbon capture and storage (CCS).

Minimizing Water Discharge and Maximizing Re-Use in Coal Combustion and Conversion Processes

William A. Shaw, HPD, a Veolia Water Solutions & Technologies Company, USA

Environmental regulation in the USA is in flux. The U.S. Environmental Protection Agency (EPA) is currently reviewing or rewriting several key regulations pertaining to the Clean Water Act. These regulations will affect the National Pollutant Discharge Elimination System (NPDES) permit program which sets discharge limits. The EPA plans to revise the steam electric effluent guidelines, which govern the standards for water discharges at coal-fired power plants, including discharges from coal ash ponds, coal piles, air pollution control systems and other sources.

When coal is burned to produce electricity, the effects on the environment extend beyond air quality. For example, the installation of wet scrubbers to remove SO₂ from air emissions also results in the capture of other pollutants such as mercury and selenium, which end up in the wastewater. Gasification of coal to produce syngas, liquid fuels, or chemicals also results in wastewater which is contaminated with by-products of the coal conversion. To protect water quality and ensure compliance with the NPDES permit, it is usually necessary to install wastewater treatment facilities at each power plant with air emission controls and at each gasification plant. As emission limits become more restrictive, and additional substances in wastewater are regulated, power plants and gasification plants will face significant additional costs to comply. In many cases new regulations will also require the need for unfamiliar or untried technologies to treat wastewater to meet revised water discharge requirements, including zero liquid discharge.

The potential impact of environmental policies on coal-fired generating plants or coal conversion plants is a material risk, and it is necessary to weigh potential operational challenges such as a reliance on new technologies against potential product cost increases and available resources. It is important to understand as much as possible the real operational challenges of new technologies and to look for ways to mitigate them, while minimizing additional CAPEX and/or OPEX. New technologies may also have an upside that must be taken into consideration. There may be opportunities to recover valuable by-products from wastewater, including the water itself.

Zero liquid discharge (ZLD) systems have been employed very successfully in US power plants for over 40 years to recover water from and eliminate discharge of cooling tower blowdown. The technology has evolved over the years, with resulting increases in efficiency and ease of operation, and lower operating cost. The application of this technology to wastewaters from coal-fired plants is very recent with only a handful of ZLD systems installed and operating over the last couple of years. Since cooling tower blowdown is very different in composition from the wastewaters generated from coal combustion or gasification, the application of ZLD technology is very different. The interest in applying this technology to eliminate wastewater discharges from coal-fired plants is high, but is seen as fraught with risk. This paper will attempt to fairly evaluate the risks and benefits of zero liquid discharge technologies in the treatment of wastewaters from coal combustion and gasification. The paper will use as examples a coal-fired power plant which installed a ZLD system to recover water and eliminate discharge of FGD scrubber blowdown, and an IGCC power plant with a ZLD system to recover water and eliminate discharge of gasifier grey water.

POSTER SESSION 1 COMBUSTION

Attrition as a Key Parameter for Evaluation of Usefulness the Oxygen Carriers in Chemical Looping Process

Ewelina Ksepko, Marek Sciazko, Olaf Piotrowski, Institute for Chemical Processing of Coal, POLAND

The Chemical Looping Combustion (CLC) is one of most promising and economically competitive combustion methods. Especially in the terms of carbon dioxide emissions reduction. The direct contact between air and fuel is avoided, and required oxygen is transported by solid oxygen carrier typically metal oxide. The significant advantage of a CLC is that a concentrated CO₂ stream can be obtained from the combustion gas stream after water condensation without requiring any energy for separation or purification. In addition, nitrogen oxide production is also greatly reduced. It can be achieved if oxygen carrier is highly reactive, of low cost, sufficient durable under repeated reduction/oxidation cycles at high temperature, with low tendency for

agglomeration, with high mechanically strength associated with high circulation of particles.

Attrition is one of the most important factors which could lead to reducing solid state oxygen carrier lifetime. Therefore the aim of the paper was to perform the procedure of oxygen carrier screening by attrition tester. Attrition was studied in room temperature in fluidized bed BAT produced by Vinci-Technologies. According to ASTM D5757-95 method attrition loss was calculated according the following equation:

$$\text{Attrition loss, \%} = \frac{m_1 - m_0 + m_5 - m'_0}{m_5} * 100$$

Where:

m[']0 = mass of second empty fines collection assembly (g),

m₅ = mass of second fines collection assembly at 5 h (g).

The five hour test showed that durability of oxygen carriers is strongly the composition and the preparation method dependent. It was concluded that bimetallic oxygen carriers based on iron oxides showed better mechanical strength comparing to monometallic once.

Our study confirmed that fluidized bed BAT tester is indeed a useful tool for determination of oxygen carrier attrition and supportive the oxygen carriers pre-selection.

Simultaneous NO_x/SO₂ Removal by Ammonia Gas Excited by Atmospheric Plasma

Shinji Kambara, Yukio Hayakawa, Kazuhiro Kumabe, Hiroshi Moritomi, Gifu University; Megumi Masui, Actree Corporation, JAPAN

The ammonia radical injection method have been developed to expand window temperature and to improve NO removal efficiency in the conventional SNCR. Ammonia radicals (NH₂) were generated by atomospheric pressure plasma. In this paper, characteristics of simultaneous NO/SO₂ removal were investigated. Both NO and SO₂ removal by the radical injection in NO/SO₂/O₂/N₂ system method were higher than that in NO//O₂/N₂ or SO₂/O₂/N₂ system. Above 90% NO removal was attained at 700°C at molar ratio of 1.5.

Application of Sewage Sludge Ashes in Chemical Looping Combustion of Solid and Gaseous Fuel

Ewelina Ksepko, Grzegorz Labojko, Marek Sciazko, Institute for Chemical Processing of Coal, POLAND

The presented paper encloses results of research on combustion technology named chemical looping combustion (CLC). The solid oxygen carriers are crucial for CLC process. Most of them are synthetic materials based on NiO, MnO₂, Fe₂O₃, CuO. Recently, some novel natural oxygen carriers (minerals, steel rolling waste etc.) according to literature are proposed, as well. The goal of paper was to prepare non expensive oxide materials (sewage sludge ashes) that might be used as oxygen carriers. Multi cycle CLC tests in TGA with this oxygen carrier have been conducted utilizing both solid (hard coal) and gaseous fuels (CH₄, H₂). One cycle test at 900°C showed that active part of sewage sludge ashes successfully reacted with coal. The revealed oxygen was fully used for coal combustion. Three cycle test with gaseous fuels showed sufficient reactivity and durability of carriers under repeated reduction/oxidation cycles at high temperature. Moreover, better reactivity and stability for natural sample of sewage sludge ash than that for synthetic one was found. Interestingly, that the oxygen transport capacity has varied depending on reaction temperature. The higher temperature the higher oxygen content was released to fuel. Both, the fractional reduction and fractional oxidation were calculated. It was found, that regeneration reaction was much faster than reduction. Mechanical strength studied by air jet attrition tester showed that sample had a more favorable abrasion performance comparing to recently known oxygen carriers. The only 1% attrition index was achieved after the five hours attrition test. Additionally, high melting temperature in reducing atmosphere was observed. According to those facts, it is concluded that waste material such as sewage sludge ashes might be successfully used in CLC process, as effective and low cost oxygen carrier. Significantly, our research showed that municipal waste after appropriate treatment might be a valuable material for energy production via coal combustion process.

W2 Wobble Plate Prime Mover - Sealed Unit

Jerry Willis, Admiral Air, Inc., USA

This paper describes recent improvements made to the design of the W2 Wobble Plate Prime Mover. Initially the W2 was conceived as an option to steam turbines as a machine for converting steam pressure and flow to torque.

Advantages were explained as follows:

The steam turbine at 90% + thermal efficiency utilizes steam velocity and pressure to drive the turbine blades. A very efficient steam turbine is teamed up with a plant to process the massive amount of steam required to operate the steam turbine. The resulting facility is approximately 35% thermally efficient.

The W2 Prime Mover at 90% + thermal efficiency in comparison utilizes only static steam pressure to produce torque by directly driving a wobble plate. Originally the

design had mechanical clearances that allowed a small amount of steam to blow through the unit. Due to the reduced steam volume required by the W2 as compared with a steam turbine an increased thermal efficiency results.

Recent advances in the design of the W2 have resulted in a sealed unit. This development allows the W2 to become competitive with industrial electric motors as well as steam turbines of all sizes.

Morphologies, X-ray Parameters, and Burnout Comparisons of Inertinite-Rich and Vitrinite-Rich South African Bituminous Coal Derived Chars

Enette Louw, Gareth D. Mitchell, Jonathan P. Mathews, The Pennsylvania State University, USA

Char structure and morphology directly influences combustion behavior as it affects the intrinsic char reactivity and reacting gas transport. In South Africa, the less reactive inertinite-rich bituminous coals are used domestically while the export market is dominated by vitrinite-rich bituminous coals. The degree of thermoplasticity during coal to char transition is strongly dependent on the petrographic composition, rank, and heating rate. These factors affect the transformations to chars of differing structures, morphologies, and hence reactivity. Here the coal to char transformations during rapid-heating pyrolysis of narrow size cuts of two South African coals were compared. These coals had different petrographic compositions but similar carbon content, vitrinite reflectance (mean-max), and organic precursors. Char samples representing different stages of mass loss were generated in a drop-tube reactor under rapid-heating conditions (10^4 – 10^5 °C/s) with a 99% N₂/1% O₂ atmosphere. The morphologies of the chars were characterized with SEM and optical microscopy, while quantitative information on the ordered nature of chars was obtained through XRD on demineralized chars. The vitrinite-rich (91.8% dmmf) coal reached a high degree of fluidity, producing mostly extensively swollen crassisphere, tenuispheres, and network-type chars. The inertinite-rich (87.7% dmmf) coal had limited fluidity which resulted only in rounding of particle edges and a large fraction of mixed-dense type chars. The final inertinite-rich char had a higher crystallite height (12.6 Å) than the final vitrinite-rich char (11.7 Å). The vitrinite-rich sample has a higher crystallite width (26.8 Å) than the inertinite-rich sample (24.5 Å). Even though these stacking parameters were similar, the inertinite-rich parent coal was significantly more ordered than the vitrinite-rich coal prior to heat treatment (11.8 Å compared to 4.3 Å), indicating a more extensive transformation for the vitrinite-rich coal. Burnout profiles obtained in a thermogravimetric analyzer at a heating rate of 5 °C/min. in air showed the inertinite-rich char had a burnout temperature of 680 °C, higher than the vitrinite-rich char's 650 °C. The temperature at the maximum rate of weight loss was at 480 °C for the vitrinite-rich char and at 530 °C for the inertinite-rich char indicating significant reactivity differences.

POSTER SESSION 2 GASIFICATION

The Design and Operational Behaviour of a Laboratory Scale Fixed-Bed Gasifier

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Coal combustion and gasification modelling approaches have been diverse and innovative in the past. With the help of modern computing capabilities it should be possible to further enhance the understanding of these highly complex processes. Research on different coals (especially on small particles of diverse nature) has been extensive. The large particle research (with all the apparent associated difficulties) is one of the many areas of modern day exploration. Single particles have been studied to determine a spectrum of characteristic behaviour. An anticipated next step is a study of reaction rates in a packed bed with wall effects taken into consideration. The heat transfer coefficient from the gas to the solid has not been conclusively studied yet and the aim of this research is to provide data of the gas composition along the length of a static fixed bed system. Also, to investigate the temperature profile, pressure drop, and the coal particle composition thereafter. This study should help fill a small gap in the lack of data for gas composition and temperature profiles in fixed a bed gasifier. The data should aid in the development of a transient model that will assist in the simulation of laboratory experiments which are difficult to operate at steady state and to describe time dependant operation of fixed bed systems.

Analyses of an Entrained-Bed Coal Gasifier Using a CFD Model Coupled with Chemical Reaction Kinetics

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A three-dimensional numerical model for the coal combustion and gasification of an entrained-bed gasification reactor has been developed by integrating the commercial computational fluid dynamic software FLUENT with the detailed kinetics modeling

software CHEMKIN. The injection system of discrete-phase fuel is employed in the simulation model. The transport exchange of mass, momentum, and energy between different phases are taken into account in the numerical model. The physical models include the turbulence model, the radiation model, and the pyrolysis model. Nine homogeneous and heterogeneous reaction equations are considered for the coal combustion and gasification processes. The proposed numerical model, which accounts for the turbulent combustion by employing the mixture-fraction approach coupled with the flamelet model, has been validated by the experimental data. Four parameters, including the wall temperature, the feeding temperature, the water addition and blend with biomass, have been examined to investigate the effects of operating conditions on the gasification process. The numerical results obtained from the present study show that a lower wall temperature leads to more production of carbon monoxide and hydrogen. It also results in a lower outlet temperature. Increasing the feeding temperature leads to a better gasification performance and a slight increase of the outlet temperature. There exists an optimal rate for the water addition in enhancing the hydrogen production. Blending the coal with biomass may lead to higher hydrogen generation and lower carbon-monoxide production in comparison with the pure coal gasification. The resulted outlet temperature is lower. An entrained-bed gasification reactor installed with a multi-stage-feeding system is also examined. The numerical result shows that the gasification performance can be improved by introducing the second feeding stage, since the extent of the temperature rising at the second feeding stage is smaller than that at the first feeding stage.

Process Modeling of H₂S Removal from Brazilian Coal Gasification Syngas with MDEA

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The Brazilian Coal Association (BCA) and the U.S. Department of Energy's National Energy Technology Laboratory (NETL) signed a Memorandum of Understanding (MOU) which reflects a mutual interest of the parties to pursue collaborative work to advance the technical, environmental, and cost performance of fossil energy technologies including gasification. Brazilian coal has very high ash and sulfur content, which present significant challenges for developing cost effective processes to make use of this natural resource. Through the MOU, researchers from BCA are working with researchers from NETL to explore ways to more effectively develop a gasification process which can provide a high quality syngas to replace dwindling local supplies of natural gas. Part of this work involves the design of a cost effective gas cleanup process. This paper presents preliminary results from modeling studies for using a MDEA-based acid gas removal process to treat syngas from the gasification of Brazilian coal. The focus of the study is to determine the minimum cost process design which meets the H₂S concentration specification in the syngas product stream and maintains a calorific value suitable for furnaces in the ceramic industry. Aspen Plus[®] has been used as the modeling environment and NETL's Modular Optimization Framework as the computational tool for optimizing the key process and equipment variables involved in the proposed system. The chemical composition of the gasification product stream was obtained from experimental results using a bubbling fluidized bed gasifier. The fuel used was coal from southern Santa Catarina State in Brazil. The layout of the resulting MDEA system is presented, which demonstrates the feasibility of using the syngas in kilns for firing ceramics.

Comparison Study on CO₂-Gasification Reactivity of Different Chars

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Coal gasification, in which coal is reacted with steam or carbon dioxide to produce a mixture of carbon monoxide and hydrogen (synthesis gas), has been intensively studied all over the world. The reaction of coal char with CO₂ is used for study of coal gasification. In this work, the comparison study was made for the CO₂-gasification reactivity of different chars included that from the different coals and under the different pyrolysis conditions as well as the coke from petroleum by the temperature-programmed reaction (TPR) technique. The results showed that the gasification reactivity of the tested chars and cokes was significantly different. The gasification reactivity of char increased as the decrease of the coal rank. The chars from the lignite have a higher reactivity than the chars from the higher rank coal or the cokes from petroleum. The gasification reactivity of the petroleum cokes is much lower than the chars from lignite and even lower than the chars from bituminous coal. It was found that the higher the pyrolysis temperature the lower the gasification reactivity. It was also found that the gasification reactivity of the coal char was greatly enhanced after the treatment by tetrahydrofuran (THF) extraction, which may be owing to the changes of the pore structure and the surface area of the coal char. In addition, the transformation of sulfur-containing gases during gasification was also investigated. Results showed that the main sulfur-containing gases were SO₂ and COS, and the release characteristic was dependent on the coal type and the sulfur forms in coal.

Determination of Kinetics of Char Gasification with Carbon Dioxide Using Thermogravimetry

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Numerous studies on the gasification of coal and char with CO₂ have been conducted in recent years; many involving the determination of kinetic parameters of this process. While other studies have employed rather complex, and computation-intensive methods for determining the kinetic parameters of this system, this study uses a far simpler and quicker means of attaining this information.

In this study, coal char is gasified in a CO₂ atmosphere under non-isothermal conditions in a TGA at different heating rates. The novelty of this study is that a model-free kinetic algorithm has been developed, based on the modification of the distributed activation energy model (DAEM) to determine the desired kinetic parameters (the algorithm is however dependent on a structural sub-model in order to determine the pre-exponential factor). Further benefit is that, once the kinetic parameters have been determined, the behavior of a particular substance at heating rates other than those used in the experiment can be predicted.

TGA data was simulated based on the random pore model using different numerical methods. The kinetics were determined using the algorithm. It was found that the algorithm was able to accurately describe the kinetics of the system, where the simulations were accurate.

Application of Pyrolytic Brown-Coal Tars in the Flotation of Black Coal

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The paper deals with research in new potential flotation agents for black coal and their comparison with an industrially applied flotation agent Montanol 508, which is used in the black coal preparation plants both in the Czech Republic and Poland. The potential flotation agents are a liquid organic phase from pyrolysis of brown coal disposed of pyrogenetic water (brown-coal tars). The experimental flotation tests are implemented using black coal samples from Darkov Mine in the CR. The effectiveness criterion of the work is to obtain flotation concentrate quality with ash content below 10 %. The results imply that it is possible to produce flotation agents from brown coal tars, which may come in useful in the flotation of black coal.

Design of an Atmospheric Bubbling Fluidized Bed for Co-Gasification of Coal and Paper Sludge

Giovanna de Simone, Stefano Cordiner, Vincenzo Mulone, University of Rome "Tor Vergata", ITALY

The co-gasification of coal and biomass is an important area of study since it would improve the overall environmental impact of the gasification technology. The coal gasification process is relatively well understood while the gasification phenomenon of biomass requires further studies due to the complexity of feedstock and the quality and compositions of the resulting syngas. Therefore, this study focuses on the gasification of one of the largely available biomass feedstock (i.e., paper sludge) in order to provide insights into its gasification phenomenon. The pulp and paper industry is an energy intensive sector and produces large quantities of biogenic waste and residuals that must be disposed in an environmentally safe way. Due to high organic content of sludge, a viable way for reduction may be based on their thermo-conversion into value-added products (i.e., syngas). Thus, paper sludge was selected as the biomass of choice for our study. Starting from the characterization and the analysis of different types of available paper sludge, in terms of heating value and composition, tests were performed on a small scale laboratory bubbling fluidized bed gasifier, showing the impact of different operating parameters including the reaction temperature, residence time, particle size distribution, and superficial gas velocity, on its performance in terms of the fluidization and mixing behaviors and the reaction conversion. Experiments were performed at both minimum fluidization velocity (U_{mf}) and 2U_{mf} under steady state conditions. Two different operating temperatures were selected: 625 and 825 °C, while the average particle size was varied from 300 to 850 μm. These findings will be used to better design gasification systems that can utilize various mixture of coal and paper sludge with reduced carbon footprints.

Carbon Dioxide Reforming of Methane Over Nanostructured Co-Ni Catalysts

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Nanostructured low percent Co-Ni catalysts on the basis of glass fibers (GF), were synthesized by "solution combustion" (SC) method. Catalytic activity of prepared samples was studied in the reaction of dry reforming of methane (DRM) with CO₂. The physico-chemical characteristics of the obtained samples were studied by the methods of XRD, TEM, TGA, AFM, H₂-TPR, DR UV-Vis. The active component was shown to be dispersed in the nearsurface layer of support as nanoparticles of 10–20 nm size,

which have a Co₃O₄ or (Co,Ni)Co₂O₄ spinel structure depending on the catalyst composition. Spinel structure of the active component strong interacting with the carrier is resistant to carbonization and provides high catalytic activity in DRM.

Methane Reforming with Carbon Dioxide Over Nickel-Uranium Catalysts

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In this work, methane reforming with carbon dioxide into synthesis gas has been performed over novel catalysts containing nickel and uranium oxides. The introduction of various amounts of uranium (5–30 wt. %) to the nickel catalyst considerably reduces the adverse effect of carbon deposits formation and increases the activity of the catalyst. The effects of CH₄/CO₂ ratio, space velocity, reaction temperature and content of uranium in the catalysts on methane conversion and the CO and H₂ yields were studied.

New Technologies for Monitoring UCG

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Underground coal gasification (UCG) eliminates the need for mining and with that the associated dangers for miners and stripping of the land. Careful monitoring of the UCG process is essential to improve process efficiency. Here we present new techniques to monitor UCG. As with all underground extraction, UCG may cause subsidence of the ground surface. Interferometric synthetic aperture radar (InSAR) is a remote sensing technique that has the capability to monitor subsidence over wide areas at a low cost. Vertical motion on the order of centimeters can be measured. Models of expected UCG subsidence are tested using various InSAR operational capabilities (frequency, mode, and repeat time) to estimate potential application. An example of UCG-related subsidence over a known UCG test site observed with InSAR is shown. The area of subsidence was approximately 400 m by 200 m with a maximum amplitude of 5 cm vertical subsidence. A second promising technique is the use of seismic data, both active and passive. A survey of possible techniques (reflection, refraction, microseismic monitoring, and in-seam) is presented along with modeling of the expected signals from typical UCG cavities. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

POSTER SESSION 3 SUSTAINABILITY AND ENVIRONMENT

A CUBIC MILE OF OIL: Realities and Options for Averting the Looming Global Energy Crisis

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A Cubic Mile of Oil is a call for an informed public debate on energy, arguably the biggest challenge we face. The book is written for an interested layperson and makes all the technical discussion accessible and relatable by dispensing with mind numbing multipliers like billions, and trillions or unfamiliar units, like Watts, barrels and Btu.

The book describes how much energy we use and from what sources, where we are headed, and what it would take to utilize alternate sources. It uses a cubic mile of oil (CMO) as the metric for comparing global energy flows from all sources.

The current global consumption of oil (ca. 80 million barrels a day) amounts to 1 cubic mile over one year. Additionally, each year the world uses 0.8 CMO of energy from coal, 0.6 from natural gas, roughly 0.2 from each of hydro, nuclear, and wind for a grand total of 3 CMO. By the middle of this century, the global energy demand is expected to rise to somewhere between 6 and 9 CMO. Where are we going to get the energy? The book goes on to describe the different energy sources, their potential, and the requirements for developing any of them to a level approaching 1 CMO/yr. Unless our solutions scale to the level of a CMO/yr, we would be just nibbling at the edges.

The book attempts to reframe the debate about energy supply, which has often been portrayed as a tension between the moral imperative of protecting the environment on the one hand and preserving the economic interests of the energy industry. This simplistic view misses the more difficult challenge that we face: namely, balancing the tension between protecting the environment—which would require us to turn off the use of fossil-fuels—against the equally important call for social justice of providing people around the world with sufficient affordable energy so they can live a healthy productive life. There are choices to be made, and the public at large must get engaged in making them.

Some Abandoned Mine Land Reclamations Practices in Turkey

Seyfi Kulaksiz, Hacettepe University; Mehmet Tombul, Pinar Bozkurt Huyuktepe, Nusret Gungor, General Directorate on Mining Affairs; Yuksel Akin, Hakki Duran, TKI; Necati Atay, Lignite Pits of Aydın, TURKEY

Mining system has been the driving force at the beginning of the history of commerce and modernization of humanity. Mining is required to sustain vital activities of human such as warm-up, shelter, transportation and for the development of civilization. Cessation of mining activities for any reason may be the end of human life, development and progress. Therefore, mining and the environment will be of equal value and must work in harmony with each other. In the studies of reclamations, it should be selected carefully and precisely that for what purpose the area will be used. The planning is needed to be done completely for reclamation of an abandoned mine land. Abandoned mine land reclamations examples of our country applications and evaluations are given in this study. Investigations were done in five mine fields. Four of the selected samples of mine reclamations were belong to industrial raw materials mine and only one mine was metallic open cast. Reclamation areas of inner and outer dumping field have been evaluated together. The selected three mine areas belong to the private sector whereas two of them are to the state enterprises. The investigated reclaimed two mine areas are continuing to support public social and economical type projects. The authors will discuss and criticize the reclamation of mined land feasible applications, regulations and their efforts from the technical point of view.

Characterization of Noise Generated by Selected Underground Mining Equipment

Marek L. Szary, Yoginder P. Chugh, Southern Illinois University; Joseph C. Hirschi, Illinois Clean Coal Institute, USA

Noise generated by mining equipment in underground room and pillar coal mines is comprised mainly from separate spectrums of three major sources: A) Continuous Mining Machines (CMM), B) Roof Bolters, and C) Haulage Equipment (cars/vehicles transporting personnel and/or coal). Spectrums from each of these major sources are also comprised from very well defined noise sub spectrums generated by individual components of the mining equipment. Noise level measurements are often presented in dBA ("A" weighted Sound Pressure Level - SPL) with frequency ranges from 100 Hz up to 10 kHz. Detailed analysis of mine noise shows that there is a relatively large component of below 100 Hz as well as above 10 kHz. Use of the "A" weighted characteristic is not feasible to measure SPL in these frequency ranges. Thus, the "C" weighted (or linear) characteristic has been used in our investigations. It has been observed that the CMM's cutter head, interacting with the coal seam using considerable thrust force and torque to extract and move coal and sometimes the rock above and below it, generates large amounts of low frequency noise (LFN). Also, during the coal extraction process, very low frequency noise (on the edge of air vibration) with high amplitude had been observed. This noise can be described as a typical LFN modulated by very low frequency, (often around or less than one hertz) and perceived as a flutter or "rambling" noise, or the product of a biting (superposition) of similar LFN spectrums. This LFN noise travels long distances in the underground mine structure. Roof bolters generate a noise spectrum with a very high frequency (above 10 kHz) component. This paper presents and discusses noise spectra's in frequency and time domains generated by underground mining equipment. These data are useful for equipment operating personnel and their supervisors and managers to properly schedule and control coal extraction and transportation processes for minimizing noise exposure.

The Activity of the Water Gas Shift Reaction over Copper Based Catalysts with Different Support

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The activity and metal-support interaction of the water gas shift (WGS) reaction over copper based catalysts with different support were studied. Five sets of samples with different support (Al_2O_3 , ZrO_2 , SiO_2 , etc.) were prepared by spray drying method for sorption-enhanced water gas shift (SEWGS) process which consists of circulating fluidized-bed reactor in pre-combustion Carbon Capture & Sequestration (CCS) technology. Catalysts were composed of copper as an active metal, supports, promoters, inorganic binders, and so on. Spray dried catalysts were calcined at 823 K under air for 3 h. The physico-chemical properties of the catalysts particle size distribution (PSD), average particle size (APS), bulk density, BET surface area, and X-ray diffraction were measured by standard methods. Especially, the attrition resistance of catalysts to apply fluidized-bed process was measured by a modified three-hole air-jet attrition tester based on the ASTM D 5757-95. The catalytic activity was investigated by multi-channel catalytic reactor. After activation for 3 h with hydrogen, WGS reaction was carried out at 573 K and 20 bar by feeding a gas mixture of H_2 , H_2O , CO with the molar ratio of $\text{H}_2\text{O}/\text{CO}=3$. The results of physical properties containing attrition resistance satisfied the basic requirements for fluidized-bed process. CO conversion rate of PC-e catalyst displayed nearly 95% at temperature of 573 K. This result suggested that the performance of the catalyst is linked to the large

surface area of the support and small CuO crystallite size through strong metal-support interaction (SMSI) between CuO and Al_2O_3 within the catalyst.

POSTER SESSION 4 CARBON MANAGEMENT

A Solid Sorbent Technique to Capture CO_2 From Flue Gas

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Carbon capture and sequestration holds the promise of continued fossil fuel usage while addressing global climate change concerns. The separation/capture step is the dominant cost in a CO_2 mitigation strategy of carbon capture and sequestration. Existing MEA wet scrubbing is energy intensive with respect to regeneration heat duty, and dry sorbent scrubbing holds the potential to lower the regeneration heat duty. Once a sorbent-based dry scrubbing process is fully investigated and any uncertainty is resolved, the technology will provide a CO_2 capture technique that is applicable to the existing fleet as well as to new coal-fired power generators. Thus, a CO_2 removal process will be available to the electric power industry that addresses capturing carbon dioxide for eventual storage.

A class of amine-enriched sorbents being investigated involves immobilized amines on supports. This type of sorbent initially used various amine-based compounds that were deposited onto a substrate. Candidate compounds included tetraethylenepentamine, pentaethylenhexamine, polyethylenimine, and others, and the supports included polymethylmethacrylate, polystyrene, and silicas. Based on screening studies, the choice materials are polyethylenimine (PEI) on silica. PEI can be linear or branched and can contain primary, secondary, and tertiary amines. Typical loadings of PEI on the silica range from 40-50% by weight and the silica has a high surface area (upwards of $300\text{-m}^2/\text{g}$). In a typical fabrication, the PEI is dissolved in an organic solvent and combined with the support in a certain ratio. The slurry is placed in a rotary evaporator resulting in the immobilization of the amine onto the support. The patented fabrication technique produced samples for the laboratory-scale testing but was also easily adapted to produce large (+600-lb) loads for subsequent larger scale testing with ADA-ES, a collaborative partner. The most recent work involves stabilization of the sorbent by using silane compounds to perform a cross-linking function.

Due to the sorbent's reactivity with CO_2 even at elevated temperatures, regeneration under an atmosphere of CO_2 is unlikely, requiring the use during regeneration of an inert sweep gas that is separable from the recovered CO_2 , i.e., steam that can be condensed. The working capacity of the sorbent at typical flue gas conditions is 3-4 mole CO_2/kg sorbent. These results have been verified by testing performed by outside organizations. Accelerated exposure testing of the sorbent with high concentrations of SO_2 (1000-ppm) and NO_x (750-ppm) poisoned the immobilized amine sorbent, revealing that for every mole of SO_2 or NO_2 that is absorbed by the sorbent, the capacity of the sorbent for CO_2 absorption decreases by a mole. It can be inferred that these type of sorbents behave similar to MEA with respect to SO_2/NO_x and that scrubbing in the form of selective catalytic reduction/flue gas desulfurization would be needed upstream of CO_2 sorbent reactors. Moisture will adsorb on the sorbent and isotherms at absorption conditions (~15% H_2O) and regeneration conditions under near pure steam surroundings have been obtained.

During the initial sorbent development studies, concerns about how the sorbents would fit into reactor schemes and into the overall power plant, in general, led to an outside study with a reactor design organization. Performance targets were established and critical information that is needed to assess the sorbents in a power plant scenario was defined. In addition, a more recent thrust has been to specify and develop information that will be required in the actual design of a reacting system, i.e. computational fluid dynamics studies.

Comparison of CO_2 from Coal Capture Processes and Valorisation Technologies to Enhance Energy Supply

Mercedes Martín-González, Carmen Clemente-Jul, Universidad Politécnica de Madrid (UPM), SPAIN

Coal is the most plentiful and evenly distributed fossil fuel worldwide. Based on current production, it is estimated that the reserves will last approximately 130 years. Its use worldwide has been increasing, mainly due to consumption by emerging countries. CO_2 emissions generated by combustion and the repercussions of such on climate change support the view that it could no longer be used. CO_2 capture may be the solution to continue using it, which would cater for the growing energy demand worldwide.

The aim of this study is to compare different processes concerning CO_2 capture that may be economically viable, ultimately showing that coal, a fossil energy source widely distributed around the world, can, as a result of using different CO_2 capture processes, be used as a clean source of electricity. Hence, in places where geological hurdles may render the costs of CO_2 storage considerably higher, since it might have to travel far, coal may be used for other purposes, thus valorizing CO_2 within the industrial sector.

This research is focused on the technical and economic comparison of the most relevant CO₂ capture projects designed in Spain using different existing technologies. The oxyfuel project in Ciuden (Leon, Spain), the IGCC Elcogas, precombustion CO₂-capture project (Puertollano, Spain) and the postcombustion project in Carboneras (Almeria, Spain) will be analyzed in order to assess the options available to valorize captured CO₂.

Valorizing captured CO₂ may be an adequate solution in areas where, although CO₂ capture is still possible, storage is not equally so, thus generating a further benefit. The possible uses of CO₂ will be assessed in vegetable growing greenhouses, harnessing CO₂ in vegetable life cycles. This will also be used in growing algae for subsequent biodiesel production.

Both CO₂ capture and valorizing will eventually lead to the clean use of coal, which will thus enhance the level of self-supply, aiding the development of electric vehicles, which require large amounts of electricity, as well as improve the level of energy autonomy in countries around the world. Another type of fuel, biodiesel, will also be obtained, without this affecting international food prices.

Carbon Capture Using Amine-Functionalized Carbon Nanotubes

Abby Kirchofer, Jennifer Wilcox, Stanford University, USA

The effect of increasing atmospheric CO₂ concentration on global warming is now recognized as one of the most important environmental issues facing society. Carbon dioxide capture and storage (CCS) is considered a primary, large-scale option for atmospheric CO₂ abatement. A major challenge in developing economically viable CCS is the need for efficient CO₂ separation from flue gases. Amine-modified carbon nanotubes (amine-CNTs) are promising sorbents for CO₂ capture from gas streams, but their high capacity is not fully understood. Coupled experimental and theoretical investigations have been carried out to investigate the CO₂ sorption capacity of amine-CNTs as a function of amine-type, CNT diameter, temperature, and partial pressure of CO₂.

Various-diameter CNTs have been functionalized with primary and tertiary amines and analyzed for CO₂ capture properties. Fixed bed extended cyclical testing was used to determine sorbent loading capacity, and thermogravimetric analysis was used to measure CO₂ loading at different temperatures and partial pressures of CO₂ in order to determine the working capacity and adsorption isotherms for the sorbents. Additionally, CNTs pre- and post-functionalization and testing were characterized using Raman spectroscopy, FT-IR, SEM, XPS, and TGA. In parallel with the experimental work, Grand Canonical Monte Carlo (GCMC) simulations of amine-functionalized sorbents were conducted. Density Functional Theory (DFT)-based electronic structure calculations were carried out to determine the geometry and charge profiles of the functionalized sorbents, which are required as input for the GCMC simulations.

Modeling CO₂ Adsorption in Micro- and Mesoporous Carbons

Yangyang Liu, Jennifer Wilcox, Stanford University, USA

To mitigate CO₂ emissions from direct combustions of fossil fuels into atmosphere, alternate energy sources with zero carbon emissions offer ultimate solutions. However, technologies based on thermodynamic efficient and large-scale economic electricity generation from non-carbon-based energy sources are still in development. Therefore, carbon capture combined with sequestration could serve as a bridging strategy to a time when noncarbon energy technologies are broadly deployed. As one of the attractive options, CO₂ captured by carbon-based sorbents as well as CO₂ sequestration in unmineable coalbeds require a thorough understanding of CO₂ adsorption properties in micro- and mesoporous carbon materials. A major obstacle is insufficient understanding of the molecular-scale processes involving CO₂ adsorption on organic matter with structural and/or chemical heterogeneities at pressures and temperatures of interest for both carbon capture and sequestration applications. Current fundamental investigations of gas adsorption onto functionalized carbon surfaces involve the characterization of carbon-based samples by experimental methods, understanding of electronic properties of functionalized carbon surfaces by density functional theory (DFT), and the thermodynamic property predictions using a Monte Carlo (MC) method within the Grand Canonical ensemble.

Complex pore structures not only for coals, but also for other carbon-based porous materials have frequently been modeled as a collection of independent, noninterconnected slit pores with perfect graphitic walls. Density functional theory (DFT) calculations including a van der Waals correction have been performed to investigate the electronic properties of the graphitic surfaces and the adsorbed phase of molecular CO₂. With a Bader charge analysis, DFT investigations also assist in setting up models for the initial framework required to carry out statistical modeling. However, the agreement between the MC and experimental adsorption experiments often involve structurally and chemically heterogeneous systems. With the chemistry of the organic matrix unknown in the current systems it is crucial that the initial models for MC are as representative of the chemistry as possible. Within the complex heterogeneous structure of the organic matrices of coal and other carbon-based porous materials, there likely exists a combination of defect sites and dangling bonds. The presence of volatile components such as water vapor, methane, and nitrogen- and sulfur-containing compounds is also expected. Indeed, these defects and functional groups are expected to play a role in the adsorption mechanisms associated with CO₂

on these systems depending on the local temperature and pressure. For instance, if the temperature and pressure conditions favor surface-bound water or various forms of dissociated water (e.g., hydroxyl or carbonyl groups at the carbon surface) at the surface this may lead to complex CO₂-water-surface interactions. Rather than CO₂ interacting directly with a surface, it may react indirectly via a shared proton. Preliminary investigation also revealed that oxygen-containing functional groups will act to enhance the CO₂-surface adsorption. Grand canonical Monte Carlo (GCMC) is employed in the next step to simulate the macroscopic adsorption thermodynamic properties. Different potential models of the CO₂ molecule are compared as well. The implementation of the GCMC method yields the adsorption isotherms of CO₂ on various functionalized carbon surfaces, as well as the selectivity for multi-component systems at various temperature/pressure conditions for both carbon capture and sequestration applications. The effects of various pore sizes, potential models, temperatures, and surface heterogeneities have been investigated. Furthermore, an algorithm of pore size distribution (PSD) optimization is developed and verified by testing several carbon-based samples on comparing the simulated adsorption isotherms with available experimental adsorption data.

Neutron Scattering Characterization of the Structure and Adsorption of Carbon Dioxide and Methane in Coals

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Using ultra small angle neutron scattering (USANS) and small-angle neutron scattering (SANS) techniques, we have studied the microstructure and the phase behavior of greenhouse gases (carbon dioxide, CO₂ and deuterated methane, CD₄) confined in pores of coals as a function of pressure. Two coal samples were selected from Illinois basin in the USA: Springfield (IN-1) and the Seelyville (Vigo 518), two samples (Callide and Gordonstone) were Australian bituminous coals. The total porosity, volume fraction of pores inaccessible to CD₄ and specific surface area (SSA) were determined using Porod Invariant analysis of the scattering curves from coals under vacuum and at zero average scattering condition, at which scattering length density of the saturating-pore fluid is equal to that of the solid coal matrix. The results indicate that all the coals exhibit surface fractal characteristics and the total porosity ranges from 7% to 12%, while the volume of inaccessible pores stays ~2%. The data analysis using the Polydisperse Sphere (PDSP) model results in the similar results. IN-1 and Callide exhibit appreciably higher SSA than that in Vigo and Gordonstone. All the coals have a broad distribution of pore sizes ranging from nanometer to micrometer pores. The in-situ measurements of the structure of CO₂ and CD₄ saturated Vigo coal were conducted in the pressure range 1 – 400 bar including the pressure that corresponds to zero average contrast condition. The adsorption process of CO₂ in all the open pores began upon the application of pressure and reaches equilibrium quickly. The scattering intensity varies progressively with pressure ranging from 0 to 345 bar in the CD₄ adsorption, which is attributed to the high compressibility of the supercritical CD₄. The process of adsorption of both gases is fully reversible and the high pressure has no impact on the coal structure.

Modeling of In-Situ CO₂ Sorption in a Fluidized Bed Coal/Biomass Gasifier

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Sorption-enhanced gasification of coal/biomass in a system of two fluidized bed reactors (a gasifier and a calciner) allows the simultaneous generation of a hydrogen stream, which is considered to be the ultimate clean fuel of the future, and a sequestration-ready CO₂ stream. In-situ CO₂ capture in the gasification reactor by the addition of a CO₂ sorbent shifts the reaction towards the production of high purity H₂, while eliminating the necessity of using the water-gas shift reactions. At the same time, releasing CO₂ in the calciner powered by oxy-fuel combustion with subsequent steam condensation allows the elimination of the high energy cost associated with gas separation. The technology thus has a great potential for relatively low cost production of a clean H₂ fuel while reducing the release of CO₂ into the atmosphere.

A collaborative research project that consists of both experimental and modeling parts is now under its way at the University of Queensland. The experimental part of the project pursues the identification of cost-effective CO₂ sorbents which demonstrate stable cyclic performance under realistic gasification conditions. The modeling part aims at the development of a comprehensive, physically-based gasifier model, which addresses the effects of CO₂ sorbent addition on the gasification processes and permits optimization of the operation and can also be used to assist reactor design.

One of the key sub-models is that describing sorption of CO₂ on a particle of sorbent material, which has a complicated pore structure. Coupling the transport through the porous medium with heterogeneous gas-to-solid reactions is essential for development of such a model. Indeed, the flux of CO₂ inside the porous particle is driven by diffusion and pressure gradients, which, in their turn, are caused by the consumption of CO₂ at the solid surfaces inside the particle. Thus, the complexities of transport modeling are coupled with those of modeling the heterogeneous reactions together with the necessity of modeling the complex pore structure of the CO₂ sorbent material.

It has been demonstrated [1] that the conventional averaging technique [2], based on the modeling of pore volume averages, neglects inter-pore transport and variations in concentrations of transported gas species within the pores. As a result, the conventional approach provides poor predictions for fast reactions, which is the case for the problem in question. Recent advances in modeling of reactive transport through porous media [1, 3] employing the conditional moment closure (CMC) methodology are used in the present study to attack the problem of modeling of CO₂ sorption on a sorbent particle. The output of this model provides a necessary input for the overall model of a fluidized bed gasifier with in-situ CO₂ capture. The poster will present the key conceptual details of our methodology and will provide preliminary comparison of model output against experimental data of CO₂ sorption rates.

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A Study on Permeability of CH₄ Pre-Adsorbed Yangquan Coal Matrix-Plug to CO₂ and He

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The CO₂ permeability of a CH₄ saturated coal matrix-plug (Ø 6 mm, length 13mm), from Yangquan, China, was studied by carrying out CO₂ breakthrough tests at 40°C. The similar tests were performed with respect to the inert gas He for comparison. The breakthrough tests were carried out in a self-confining flow cell equipped with an online thermal conductivity detector for continuous monitoring the CO₂ or He signal. The retention of gas by coal and the influence of the pore gas pressure were investigated. It was found that unlike He there was significant residual CO₂ left in the coal matrix even after CO₂ was flushed by CH₄ for 36 hours. It reveals that coal has a relative stronger retention capacity for CO₂, which leads to the difference in its breakthrough time for different CH₄ flushing time. No notable residual He was found during the breakthrough tests. The He permeability of the test coal plug was found to be significantly higher than for CO₂. The obtained permeability coefficients of the coal plug with respect to CO₂ or He at steady state are similar for the repeat breakthrough tests. This implies that no significant structural changes occurred during the tests. The permeability coefficients varied with pore gas pressure due to changes in pore wall interactions (Klinkenberg effect), the swelling of coal and the adsorption boundary layer.

CO₂/NO_x Decomposition via ODF Electrodes using Solid Oxide Electrolyser Cell

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Oxygen-Deficient Ferrite (ODF) electrodes are integrated with Solid Oxide Electrolyser Cell (SOEC) to decompose carbon dioxide (CO₂) into carbon (C) or carbon monoxide (CO) and oxygen (O₂), while NO_x can also be decomposed into N₂ and O₂. The cells are tested in a NexTech Probostate™ apparatus combined with EIS/potentiostat and gas chromatography (GC). In our preliminary tests, we detected high percentages of CO/N₂ and O₂, at the cathode and anode sides flue gases respectively, when CO₂/NO_x was fed to the cathode side and a small potential bias applied across the electrodes. Depending on the applied potential, the system is capable of decomposing CO₂ into C or CO. Through the in-situ EIS and exhaust gas analyses, and post-test study such as SEM, XRD, XPS of the ODF the capability and efficiency of CO₂/NO_x decomposition are currently being evaluated.

A Detailed Well Log and 3D Seismic Based Interpretation of the Fruitland Formation: San Juan Basin Carbon Sequestration Pilot Site

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The Fruitland Formation of the San Juan Basin in New Mexico and Colorado was deposited along the western coast of the late Cretaceous Western Interior Seaway. In this study we present a detailed characterization of the Fruitland Formation in the area surrounding the Southwest Regional Partnerships' San Juan Basin carbon sequestration pilot site. The project is funded by the U.S. Department of Energy and is managed by the National Energy Technology Laboratory. The study incorporates well logs from 39 wells and 9 square miles of 3D seismic data in the area surrounding the CO₂ injection well. Interpretation suggests the presence of 4-5 coal seams within the Fruitland Formation at the site. The basal Fruitland coal consists of two coal zones (lower coals

A and B with thicknesses of 10ft. to 13ft.) that are separated by a thin shale layer approximately 2ft. thick. The middle Fruitland coal consists of a single coal zone roughly 10 feet thick through the area. The upper coal seam is the most heterogeneous and hardest to resolve in the log displays. The upper coal appears to split northeast of the injection well.

The well log interpretations form the basis for additional interpretations of the 3D seismic data over the area. The integrated well log and 3D seismic study will provide one of the most detailed views of the Fruitland coal systems in the basin. 2D synthetic seismic models will be developed to test hypotheses about interrelationships between coal distribution and seismic response and to help validate seismic interpretations. Attribute analysis will help identify changes in coal properties and enhance possible faults and fracture zones in the reservoir and sealing strata that could serve as CO₂ leakage pathways. This study will delineate structural and stratigraphic properties that could have significant influence on reservoir behavior. The study will provide the basis for better estimates of coal volume and heterogeneity, flow path distribution and storage capacity, and potential locations of leakage pathways. The results will be useful for the development of second generation reservoir models.

Development of a 3D Grid, Fracture and Property Models for the Upper Freeport Coal and Overburden Using 3D Seismic: Marshall County West Virginia Pilot Sequestration Site

Tom Wilson, Lierong Zhu, Richard A. Bajura, West Virginia University; Richard A. Winschel, James E. Locke, CONSOL Energy Inc., USA

Discrete fracture networks within a CO₂ injection zone (the Upper Freeport coal) and overlying sealing strata are developed stochastically and distributed through the subsurface using 3D seismic attributes as drivers to obtain directional permeabilities, sigma factor and porosity associated with the fracture network. CO₂ injection at the Marshall County, West Virginia, carbon sequestration pilot site is underway to test the feasibility of combined carbon sequestration and enhanced coal bed methane recovery in unminable coal seams. The pilot test is being conducted by CONSOL Energy Inc. Several site characterization and monitoring activities are proceeding at the site in collaboration with West Virginia University and National Energy Technology Laboratory researchers. In this pilot test, CO₂ is injected into unminable regions of the Upper Freeport coal seam in southeastern Marshall Co. The site lies within a 1km² area that is outlined by production laterals along its perimeter. As part of this effort a 3D seismic (swath) survey was acquired over the site. A synthetic seismogram developed from sonic and density logs collected at the site provides the connection between seismic reflection events and subsurface geology. Formation top depths obtained from vertical and lateral wells at the site provide a detailed view of subsurface structure. Subsurface structure maps provide the basis for a time-depth function which was used to convert the 3D seismic time volume to depth. Interpreted reflection events were picked in intervals extending from about 600 feet above sea level to approximately 1300 feet below sea level. The event at 600 feet corresponds roughly to the Waynesburg A coal seam and the event 1300 feet below sea level, corresponds to the Big Lime or Greenbrier Limestone. The Upper Freeport seam lies roughly 1300 feet beneath the surface at the site (~ 330 feet below sea level) and the overlying Pittsburgh seam lies roughly 700 feet beneath the surface (~ 270 above sea level).

A 3D model grid was developed using cells 20 feet x 20 feet in the horizontal plane and approximately 20 feet in the vertical dimension. Grid cell thickness in the Pittsburgh and Upper Freeport coal seams was set at 8 feet and 5 feet, respectively. Post stack processing (attribute analysis) was used to enhance and identify subtle discontinuities in the seismic data that may be related to field-scale faults and fracture zones. The layered model is populated with fractures and cleats. Some general assumptions are made about cleat dimension and aperture distribution based on the literature. A power law length distribution is assumed. Aperture is assumed to be proportional to fracture and cleat length. A power law distribution is also inferred for attribute-derived discontinuities in the 3D seismic. Spatial variations in fracture intensity are distributed through the model using a 3D seismic measure of localized structural discontinuity. Permeabilities in the i, j, and k directions, sigma lengths in the i, j and k directions, along with sigma factor and porosity of the discrete fracture network are calculated for each grid cell in the model, which extends from the Upper Freeport injection seam through several intervals in the overlying sealing strata across the northern injection laterals at the site. The model identifies areas within the reservoir most likely to be impacted by CO₂ injection and migration. The model will also help focus the results of time-lapse processing and interpretation in high permeability and porosity regions where the greatest probability for change of acoustic properties in response to CO₂ injection and methane production is likely to occur.

Development of Highly Efficient Absorbents for Post-Combustion Capture

Jae Goo Shim, Ji Hyun Lee, In Young Lee, Jun-Han Kim, No-Sang Kwak, Young-Seok Ehom, Kyung Ryong Jang, Green Growth Laboratory, KEPKO Research Institute, KOREA

Highly efficient amine absorbents for CO₂ capture from the flue gas of coal fired power station were developed. The development of absorbent for CO₂ capture is one of the core technologies in the manner of chemical absorption. The newly developed absorbents (KoSol series) have been evaluated their capability for CO₂ capture through

the extensive absorbent screening, a vapor-liquid equilibrium test and a bench scale continuous operation (2 Nm³/hr) test. After lab-scale verification of absorbent capacity, continuous operation of CO₂ capture test bed which could treat 2 ton CO₂/day in the flue gas from the coal fired power station was performed. For the comparison of absorbent capacity, Monoethanolamine (MEA) which is the representative chemical absorbent for CO₂ separation is tested followed by newly developed absorbent (KoSol-3). Based on the continuous operation data, we have analyzed the operation characteristics of the each absorbent including temperature of the absorber and stripper, CO₂ lean/rich loading values. In addition, we have evaluated the energy requirement for regeneration of the absorbent and the degree of CO₂ removal. It was observed that compared to the MEA, the regeneration energy using KoSol-3 was reduced drastically and it was found less corrosive than MEA.

Screening of Sulfur Resistant Solid Sorbent for CO₂ Capture from Coal Power Plant

Joong Beom Lee, Tae Hyoung Eom, Dong-Hyeok Choi, Bok Suk Oh, Jeom In Baek, Kyeongsook Kim, Young Ho Wi, Chong Kul Ryu, KEPCO Research Institute, KOREA

Regenerable solid sorbent technology is one of the emerging technologies as a cost-effective and energy-efficient technology for CO₂ capture from flue gas. The objective of the study is to identify and evaluate solid sorbents that potentially could be utilized in a dry CO₂ capture process using regenerable solid sorbent. This paper summarizes the results of performance of solid sorbent for CO₂ capture using simulated flue gas containing sulfur dioxide. Various dry regenerable CO₂ sorbents were prepared by spray-drying techniques to evaluate their effect of sulfur resistance on various matrices. Each sorbents contained 35~50 wt% of potassium carbonate as an active. The physical properties, particle size distribution and average particle size, bulk density, BET, Hg porosity and shape, of the spray-dried sorbents were investigated by standard methods and the attrition resistance of the sorbents for circulating fluidized-bed application was measured with a modified three-hole air-jet attrition tester based on the ASTM D 5757-95. Sorbent chemical reactivity was measured in low temperature range (carbonation at 70°C and regeneration at 120°C~140°C) with simulated flue gas containing 50 ppm SO₂ with simultaneous thermo gravimetric analyzer (TGA). The maximum CO₂ sorption capacities of sorbent was approximately 9wt% with simulated flue gas containing 50 ppm SO₂ and attrition index (AI) reached below 15%. The results of physical properties and CO₂ sorption capacities showed excellent characteristics for circulating fluidized-bed process application to capture CO₂ from flue gas condition.

Solid Sorbents for Sorption Enhanced Water Gas Shift (SEWGS) Reaction to Capture CO₂ from Syngas

Tae Hyoung Eom, Joong Beom Lee, Dong-Hyeok Choi, Keun Woo Park, Jeom In Baek, Seong Jegarl, Chong Kul Ryu, KEPCO Research Institute, KOREA

Integrated gasification combined cycle (IGCC) integrated with carbon capture and storage (CCS) has been regarded as a promising option to reduce CO₂ among fossil fuels for the electricity-generating units. The new concept for the pre-combustion CO₂ capture process proposed by KEPCO Research Institute, which is named as one loop sorption enhanced water gas shift (SEWGS) process, is one of the promising capture technologies. The SEWGS process is combined the water-gas shift reaction with CO₂ capture at the same time in the process consisted of two fluidized-bed reactors. In this study, some promoted MgO-based dry regenerable CO₂ sorbents prepared by spray-drying technique were characterized to evaluate their applicability for SEWGS process. The sorbents were composed of MgO as an active component, supports, promoters, inorganic binders, and so on. Spray dried catalysts were calcined at 773, 823, 873, 923 K under air for 3 h. The MgO-based sorbents satisfied most of the physical requirements, a shape, an average size and a size distribution and a bulk density, for commercial fluidized-bed reactor process along with reasonable chemical reactivity. Maximum CO₂ sorption capacity in the middle of the spray dried solid sorbents was approximately 13.9 mg-CO₂/g-sorbents at 473 K and 20 bar with synthesis gas conditions and some of sorbents showed to reach the initial sorption capacity for multi cycle. These properties are suitable for fluidized one loop SEWGS process.

Investigation of Sorption Enhanced Steam Hydrogasification of Coal for In Situ Removal of CO₂ and Self-Sustained Hydrogen Supply

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The in situ removal of CO₂ and the enhancement of the energetic gas yield including hydrogen and methane by sorption enhanced steam hydrogasification (SE-SHR) process were investigated experimentally. Lignite was used in this study as the feedstock for steam hydrogasification reaction (SHR) with the addition of calcined dolomite as sorbent. CO₂ was almost reduced to zero with the introduction of the sorbent into the reactor. The production of hydrogen and methane was increased simultaneously. The hydrogen yield was augmented by 60% when the mass ratio of

sorbent to coal was increased to 3 as compared with the SHR without sorbent. The hydrogen in the product gas was sufficient to maintain a self-sustained supply back to the SHR when the sorbent/coal mass ratio was over 1. The sorption enhanced performance was determined at different temperatures ranging from 650°C to 800°C and at other different experimental parameters. These results will be presented. The main conclusion of this study is that the overall performance of the SE-SHR was substantially improved compared to the conventional operation of the SHR.

POSTER SESSION 5 COAL-DERIVED PRODUCTS

Study to Direct Liquefaction of Mongolian Brown Coal Samples

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Mongolia is included in the list of ten world countries, which have great natural wealth and coal resources. Mongolia's total inferred coal resources are as predicted around 150 billion tons. Oil supply security and price concerns have led to a renewed interest in coal as an alternative feedstock for the production of transport fuels and chemicals. By using coal conversion technologies, such as coal-to-liquids (CTL), the world's vast coal resources could become an important alternative to crude oil.

This paper was focused on the study of direct liquefaction of three kinds of coal. First the chemical analysis such as a determination of ash content, moisture, and volatile compound, contents of carbon, hydrogen, nitrogen and sulfur was carried out. The direct liquefaction of coal samples was studied in a shake-slurry reactor in presence of different solvents like heating oil and tetralin under the same conditions of temperature in range of 300-450°C, hydrogen pressure of 80-100 bar.

Modifying Petroleum Paving Asphalt by Coal Liquefaction Residues

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Direct coal liquefaction (DCL) is one of the processes for the production of clean fuels from coal. While it also produces 25-30% residues. Better use of the coal liquefaction residue (CLR) is important to the overall economy of DCL process. Four coal liquefaction residues from the different coal or the different units, named as CLR1, CLR2, CLR3 and CLR4, were used in this study. The modified bitumens were prepared by blending the residue (7 wt %) with the base bitumen (BZ90) under the same conditions. The standard tests for the base and the modified bitumen were carried out following JTJ 052-2000 standard (Chinese standard), which is compatible with corresponding ASTM standard. The CLR1 appears with the highest hexane-soluble fraction (HS) content and the lowest tetrahydrofuran-insoluble fraction (THFIS). The CLR4 appears with the lowest content HS and the highest THFIS content. The CLR2 appears with the lowest toluene-insoluble/tetrahydrofuran-soluble fraction (PA) content. The CLR3 and CLR4 appear with the highest PA content. The CLR2 appears with the lowest PA content. Addition 7% of the residues in BZ90 led to the similar change with respect to the softening point and the penetration value but significant difference in the ductility. Addition of CLR2 and CLR4 resulted in the less decrease in the ductility than the addition of the other two CLRs. There is notable difference in the morphology of four modified bitumens, but the TFOT process seems make no notable change in the morphology of the same CLR-modified bitumen. The order of the ductility of the modified bitumen is agreed with uniformity of the modified bitumen and the size of the residual in the modified bitumen but not the size of the original CLR. During the blending process the size of the CLR decreased in some extent depending on the nature of the CLR. The tetrahydrofuran-insoluble fraction (THFS) of CLR2 or CLR4 with less amount of higher molecular weight fraction may more easily dissolve into the base bitumen than that of CLR1 or CLR3, resulting in positive effect on the ductility of the modified bitumen. Considering all these facts, the moderate content of HS, PA and THFIS fractions, the higher content of hexane-insoluble/toluene-soluble fraction (A) and lower molecule weight of THFS made CLR2 is the best bitumen additive.

Viscosity Characteristic of Coal-Oil Slurry with High Inertinite Content

Ke Zheng, Shansong Gao, Ke Wu, Dexiang Zhang, East China University of Science and Technology, CHINA

Viscosity characteristic of coal-oil slurry plays a very essential part in direct coal liquefaction process and it can influence on the abilities of coal-oil slurry's transportation and liquefaction. For future industrial application, the viscosity changes of three types ShenHua coal-oil slurries with different contents of inertinite (SHB,SHV,SHG) were observed by the high temperature viscometer on condition of rising temperature (from 40°C to 240°C) and atmosphere. The effects of temperature, heating rate, solvent properties, coal/solvent ratio and coal kind on the viscosity of coal-oil slurry were investigated. The result shows that temperature is one of the important factors, all coal-oil slurries' viscosities decreased firstly at lower

temperature, then stayed invariable at medium temperature, finally increased at higher temperature as temperature rising. Such as when the heating rate is 5°C /min, the viscosity of coal-oil slurry with 45% of SHB was 188mPa·s at 40°C, then decreased until it reached 86mPa·s at 160°C and remained stable with a slight change, but it began to increase after 220°C and reached 94mPa·s at 240°C. This phenomenon was caused by the co-action of solvent's decreasing viscosity and coal swelling. The viscosities of coal-oil slurries rose with increasing coal/solvent ratio. Meanwhile the viscosity curve of coal-oil slurry became sharper and its stable part became shorter, as well as the temperature at where the viscosity of coal-oil slurry started increasing got declined. At the same coal/solvent ratio, both measures of increasing heating rate and solvent amount can lower the viscosity of coal-oil slurries within a certain range. By comparing there different coals, the result shows that the viscosity of ShenHua coal-oil slurries with high inertinite is the biggest on the same condition. Such as on the condition of 9/11 ratio (45%), 5°C /min heating rate and 40°C, the viscosity of SHB slurry was 188mPa·s and SHV was 217mPa·s, but the viscosity of SHG slurry which has the highest inertinite content was 259mPa·s. And the temperature of rising point in viscosity change curve of SHG slurry is the lowest on the same condition. That is because after vacuum drying, high content of moisture in SHG caused high porosity and it contained more solvent in coal particle when it mixed with solvent, so high inertinite content coal can increase the viscosity of coal-oil slurry.

Fischer-Tropsch Process: Impact of Hydrocracker Model Rigor
Seethamraju Srinivas, Randall Field, Howard J. Herzog, MIT Energy Initiative, USA

The hydrocracker is an important part of a Fischer-Tropsch (FT) plant which catalytically cracks the wax from FT reactor in the presence of H₂ to yield components in the naphtha and diesel range. The modeling of a hydrocracker is challenging in terms of the number of components involved, the reaction kinetics and the phase equilibrium aspects owing to the gas-solid-liquid reactions present. In the present work, we investigate the consequences of number of components considered and the presence of isomers on the resultant product distribution. Results of the simulations for a combination of the following cases are presented – paraffins considered with no lumping, different lumping schemes with 3 to 5 components present in a lump and the presence of isomers. The resulting variation in the cracker performance and product quality (ASTM D86 curve) are elucidated.

Calcium Looping Process (CLP) for Clean H₂ and Electricity Production from Coal: Design and Operation of the Sub-Pilot Scale Carbonator
Nihar Phalak, Shwetha Ramkumar, Niranjani Deshpande, Yao Wang, William Wang, L. S. Fan, The Ohio State University, USA

The Calcium Looping Process (CLP) is one of the clean coal technologies being developed for the production of hydrogen (H₂) and electricity from coal-derived syngas. It integrates the water-gas shift (WGS) reaction with in-situ carbon dioxide (CO₂), sulfur, and halide removal in a single-stage reactor. In the CLP, a regenerable calcium-based sorbent is used to chemically absorb CO₂, sulfur, and halide impurities from the synthesis gas during the production of hydrogen. The removal of CO₂ drives the water-gas shift reaction forward via Le Chatelier's principle, obviating the need for WGS catalyst and enabling the production of high-purity hydrogen. The spent sorbent is heated in a calciner to regenerate CaO for reuse in the process and to release a concentrated CO₂ stream that can be dried and sequestered. Overall CO₂ emissions from the process are essentially zero. The regenerated sorbent is reactivated in a hydrator, to reverse the effect of sintering and improve the recyclability of the sorbent, before being reintroduced into the hydrogen production reactor – carbonator. The high temperature operation of the three CLP reactors allows the utilization of high quality heat for electricity production. This significantly reduces the energy penalty associated with CO₂ capture.

Experiments conducted in a laboratory-scale fixed bed reactor have shown that production of high purity H₂ with in-situ CO₂ and contaminant removal is possible at low steam to carbon ratio (1:1) and moderate pressures (3-5 atm). Based on these results, a 25 kWth fluidized bed carbonator has been designed and constructed at The Ohio State University (OSU). Studies on gas-solid flow and operating regime of the carbonator have been conducted on a cold flow model of identical dimensions. Hot flow testing in the 25 kWth carbonator has also been conducted. These results will be presented and plans for future work will be briefly highlighted.

The Possibility of Utilization of Carbon Black from Pyrolysis of Municipal Waste

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The content of inorganic component – ash in biomass forms the principal limiting factor of further utilization of pyrolytic carbon. The content of ash depends on the nature of input materials. The wrong sorted biodegradable municipal waste can contain up to 50 % of inorganic component from which soil particles (quartz, plagioclase, muscovite, calcite) form approximately 30 %. The pyrolytic products of waste can be used as a source of energy, however pyrolytical carbon can concentrate non-desirable elements: sulphur, chlorine and heavy metals with exception of copper and cadmium.

The sample of municipal waste for pyrolysis contained 14.3 wt % of ash which was concentrated up to 40 – 46% in dependence of moisture of pyrolyzed material. The ash content in pyrolytic carbon is increasing with increasing moisture of municipal waste approximately by 1 % per 10 % moisture. On the contrary, content of carbon, hydrogen and nitrogen decrease with increasing moisture of municipal waste. The content of hydrogen in pyrolytic carbon of dehydrated municipal waste was 2.5% , in municipal waste of moisture 65 % it was 1.4 respectively. The corresponding values for nitrogen were 1.6 and 1.3 respectively. The content of carbon decreases from 49 to 44.5 %. Calorific value decreases with decrease of carbon content from 17.4 MJ/kg down to 15.5 MJ/kg. Concentrations of chlorine and sulphur are important among energy parameters. Content of chlorine in pyrolytic carbon was in range from 0.61 to 0.76 % which corresponds to the usual concentrations of chlorine in coal. The concentration of sulphur is relatively low – 0.3 %.

Calorific value as well as concentration of potentially toxic elements (chlorine, sulphur) show that energy utilization of pyrolytic carbon for energy production is possible, however, the high content of ash is disadvantage. The method of X-ray diffraction was used for quantitative determination of the main mineral phases which are not dependant on moisture of pyrolyzed waste. The most important phases are calcite (13.9 – 15.0 %) and quartz (5.8 – 7.4 %). Other identified phases are presented as minor components: rutile (TiO₂) 0.42 – 0.82 %, sylvite (KCl) 0.99 – 1.31 % and magnetite (0.69%). Rutile occurs in pyrolytic coke as products of pyrolysis of plastics in which it is used as component of pigments. From the phase analysis it results that high content of ash in pyrolytic carbon can be decreased to 32 – 36 % using leaching in HCl. After decomposition of calcite, in pyrolytic carbon it remains free CaO (up to 8.2 %) which can have desulfurisation effect. The pyrolytic carbon can be processed and modified by opening of pores which improves also its sorption properties and then it can be used as a filler or sorbent.

**POSTER SESSION 6
COAL SCIENCE**

Pyrite and Trace Element Associations in Waterberg Coals, South Africa
NJ Wagner, University of the Witwatersrand, SOUTH AFRICA

Coal is set to remain the dominant source of fuel for South Africa for the foreseeable future, generating around 88% of the electricity. Low-grade coals are being used in increasing amounts for power generation, and with the increased ash content come increased sulphur and other potential pollutants bound within the coal. Potential pollutants in coal can be removed post-utilization, during and pre-utilization. Pre-combustion desulphurisation (primarily in the form of pyrite reduction via destoning) may not currently be deemed economically viable due to the associated carbon loss (carbon = money). However, if it could be demonstrated that other harmful pollutants (such as Hg, As, Se, to name a few) are removed at the same time as pyrite-rich coal particles, pre-utilization clean-up for sulphur and hazardous air pollutants could become a feasible option, despite the carbon loss. In literature there is generally a positive correlation between pyrite and certain hazardous volatile trace elements, specifically As and Hg. As volatile trace elements (Hg, As, Se and Cd) frequently escape complete capture in pollution control devices, it may be beneficial to remove these elements prior to combustion. There have been several studies on trace elements in South African coals, but no detailed study on the Waterberg coal field. Certain South African studies attempted to determine the mode of occurrence of specific trace elements in Witbank and Highveld coals, but specific correlations between pyrite and volatile trace elements were not drawn. In the current research, coals from the Waterberg coalfield, South Africa, were density separated to achieve samples with concentrated pyrite / elevated sulphur contents. The run-of-mine coals reported sulphur values ranging from 1.4 to 1.6%, and separated sink products (specific gravity of 2.4 g/cm³) ranged from 2.4 to 33.4% total sulphur. The sample (5b2.4s) that reported the greatest concentration of total sulphur, reported 63% by volume pyrite as observed petrographically (maceral group analysis including mineral matter), 25% FeS₂ (sulphur form analysis), 64% Fe₂O₃ (XRF analysis), with an ash content of 65% (a.d.). The trace element analysis, conducted by ICP-MS, reported extremely high levels of Hg and As; 9.79 and 121 mg/kg respectively. The parent sample reported Hg values of 1.39 mg/kg and As values of 8.45mg/kg. Thus it would appear that there is a correlation between pyrite content and Hg and As, although data interpretation is ongoing. There were slight increases in concentration in Se and Cd between the 5b parent and 2.4 sink product, indicating that these two elements are unlikely to be associated with pyrite.

Briquetting of Tunçbilek Lignite

Ufuk Gunduz, Ozkan Murat Dogan, Bekir Zuhtu Uysal, Gazi University; Selahaddin Anac, Mustafa Ozdingis, TKI, TURKEY

Briquetting of coal has been a very widely used technology since nineteenth century. The selection of binders for the production of smokeless fuel briquettes from various coals has been largely empirical relying on simple physical test methods. It is

necessary to optimize the briquetting process because of the increasing environmental constraints on coal utilization.

Turkish lignites are known as very difficult for briquetting. The Turkish Coal Enterprises has been working on a project for the production of briquettes by using different binders for various coals. It is known that many materials are used as coal briquette binders, such as coal tar, coal pitch, petroleum residues, starch, synthetic organic polymers, molasses, and inorganic materials of lime, ceramic, clay, etc.

In this work, briquettes using Tunçbilek lignite were prepared in our laboratory. Turkish lignite was first mixed with molasses. The amount of molasses used in the studies was 10 % (w/w) of the lignite. The other chemicals used in the preparation of briquettes were asphaltite (20 %), lime (3 %) and some binding additives. The compositions are as weight percentages. The mixtures were then briquetted under a pressure of 140 MPa with a Sematron press. The briquettes had a cylindrical shape, 30mmx10mm (dxh). Mechanical tests with the produced briquettes were carried out with the same press. The briquette was inserted between the two boards of the press and the boards were pushed to each other to determine the force necessary for briquette destruction. This test was performed with dry briquettes and also with briquettes which were kept in water for an hour.

Turkish Standards Institution (TS 12055) states the mechanical strengths and water resistance of Class I briquettes as 130 kg/cm² and 70 %, respectively, and of Class II briquettes as 100 kg/cm² and 70 %, respectively. With the briquettes produced at room temperature and cured at 100 °C for one hour, Class I requirements were achieved.

Swelling Behavior of Coal in Solvent under Elevated Temperature and Pressure by a Linear Variable Differential Transformer Deformation Transducer

Jianli Yang, Lei Chen, Yongwang Li, Institute of Coal Chemistry, Chinese Academy of Sciences, CHINA

Quantification of coal swelling in solvent has attracted attention due to it closely related to coal conversion process, especially coal liquefaction and pretreatment. Understanding the change of the coal in solvent with temperature under pressure is essential for optimizing the coal slurry preparation condition and developing the efficient coal conversion process. In this study, a linear variable differential transformer (LVDT) deformation transducer is used to characterize the swelling behavior of eight Chinese coals (from lignite to anthracite) in two solvents under elevated temperature and pressure. A coal liquefaction process derived recycled oil (Oil) and pure tetralin (THN) are used as the test solvents. The experimental temperature and pressure used in this study are 50-400 °C and 1 MPa N₂ (initial). The swelling ratios of coals in Oil increased as the increase of temperature and peaked at 300 °C for lignite L1, 300°C for lignite L2, and 250°C for lignite L3, respectively. Similarly, the swelling ratios of bituminous coals in Oil increased as the increase of temperature and peaked at 300°C for bituminous coal B1, 350°C for bituminous coal B2, and 300°C for bituminous coal B3, respectively. However, the swelling ratios for anthracites A1 and A2 in Oil increased as the increase of temperature and kept increase continuously in the temperature range tested. The swelling ratios of bituminous coals in solvent are generally higher than that for lignite and anthracite. The swelling behavior of the coal chars (treated coal under inert gas and elevated temperatures) for bituminous coal B3 was also investigated. The swelling ratio of 150°C and 350°C chars in THN increased as the increase of the swelling temperature and peaked at 300°C and 350°C, respectively. No significant swelling in THN was observed for the char obtained by thermal treatment of coal B3 at 550°C.

Characterization of Reacted Coal Chars using Ion Beam Techniques (PIXE and STIM)

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Proton micro beam (H⁺ - 2.8 MeV) was used as a probe for computed tomography for 3D characterization of coal and reacted coal chars. Scanning transmission ion microscopy (STIM) and Particle induced X-ray emission (PIXE) were performed at the recent installation of ultra - stable single - ended HVEE 3.5MV SingletronTM accelerator at the CENBG. The experiments were planned to acquire mass density distribution and elemental composition in the test samples. The aim of the experiment was to compare and contrast the difference between the surface morphology of coal (as received) and remains of the reacted coal chars obtained upon gasification with carbon dioxide under high pressure conditions (25 bars). The slice by slice analysis using ion beam technique is likely to present the elemental mapping of the non-carbon content, which often poses a hindrance in the flow of the reactant gas to the active carbon site, often a main factor for diffusion limitation case. Also, time scale variation of the receding reaction interphase, showing changing orientation of cleats and fractures during carbon dioxide reaction will be shown.

Mercury Oxidation, Transformation and Removal in Flue Gas of Five Chinese Coal-Fired Power Plants

Yufeng Duan, Liguang Yang, Yunjun Wang, Xianghua Yang, Southeast University; Yuqun Zhuo, Lei Chen, Liang Zhang, Tsinghua University, CHINA

Mercury speciation and emission from five coal-fired power plants in China were investigated. The US-EPA recommended Ontario Hydro Method (OHM) was used in flue gas mercury sampling before and after fabric filter (FF), electrostatic precipitator (ESP) and wet flue gas desulphurization (WFGD) locations. Mercury speciation Hg⁰, Hg²⁺ and Hg^P in flue gas was analyzed by ASTM D6784 02. The solid sample, such as coal, bottom ash and FF/ESP ash were analyzed by DMA 80 based on EPA Method 7473. It could draw out that: (1) the mercury speciation varied greatly when flue gas going through FF and ESP. Of the total mercury in flue gas, the proportion of Hg²⁺ ranged from 4.87%-50.93% before ESP and 2.02%-75.55% after ESP, while that of the Hg⁰ was in the range of 13.81%-94.79% before ESP and 15.69%-98% after ESP, as well as that of the Hg^P was in 0%-45.13% before ESP and 0%-11.03% after ESP. (2) The mercury in flue gas mainly existed in the form of Hg⁰ and Hg²⁺. (3) The concentrations of chlorine and sulfur in coal, NO_x, SO₂, HCl and Cl₂ in flue gas have positive correlation to formation of the oxidized mercury. (4) It was found that the mercury removal rate increases when the contents of chlorine and sulfur in coals are more.

Synthesis of Nanoporous Carbon Materials from Modified Coals and Cokes

A.V. Samarov, Ch.N. Barnakov, A.P. Kozlov, Z.R. Ismagilov, Institute of Coal Chemistry and Material Science; M.A. Kerzhentsev, Boreskov Institute of Catalysis, RUSSIA

A known efficient adsorbent AX-21 was produced by oxidation of carbon containing materials – coals and cokes by nitric acid, mixing of formed aromatic acids with hydroxides of metals of Groups Ia and IIa of the Periodic Table and pyrolysis of the mixture in the inert atmosphere at 700-900°C [1, 2]. We have developed a different method of the adsorbent preparation [3], in which, instead of oxidation with nitric acid, sulfuration of the precursor with concentrated sulfuric acid was used. The obtained material has similar characteristics and in accordance with the present day terminology is regarded as a nanoporous carbon material.

It was established that this nanoporous carbon material, depending on the duration or temperature of the carbonization, had either one-dimensional or three-dimensional hopping conductivity with variable hop length, described by the Mott law. Possibility of low temperature (400-900°C) graphitization of the material with one-dimensional conductivity was shown. The use of the nanoporous material for stabilization of nanoparticles of 3d metals of iron group was demonstrated. The magnetometric measurements showed that the metal particles were in the ferromagnetic state and were characterized by a high field of the local magnetic anisotropy. High potential of the use of this nanoporous carbon material as the support for PEMFC cathode catalysts was demonstrated.

1. US Patent No 3624004.
2. US Patent No 4082694.
3. RU Patent No 2206394.

The Waste Rock Application in Hydric Reclamation, Czech Republic

Eva Pertile, Peter Fecko, Martina Brezinova, Michal Guziurek, Lucie Nezvalova, Barbora Molinova, Vojtech Dimer, VŠB – TU Ostrava, CZECH REPUBLIC

The evaluation of the impact of waste rock application in hydric reclamation of natural water-bearing subsidence troughs in the Karviná Region was carried out in sixteen localities where waste rock had been used in the past for the purposes of bank system improvement. Within the evaluation of waste rock impact on the hydrochemical character of water in the subsidence troughs the values of geochemical background were identified. In order to compare the impact of waste rock on the quality of water, changes in the hydrochemical parameters were monitored in the localities without waste rock banking, with partial (maximum 1/2 circumference) and complete waste rock banking. Within the evaluation of waste rock impact on the hydrochemical character of water in subsidence troughs, values of geochemical background were determined as an arithmetic mean adding or subtracting a standard deviation.

Influence of the Graphitization Degree and Presence of 3D Metals of Iron Subgroup on the Reactivity of Carbon Materials

Ch.N. Barnakov, G.P. Khokhlova, Z.R. Ismagilov, Institute of Coal Chemistry and Material Science; M.A. Kerzhentsev, Boreskov Institute of Catalysis, RUSSIA

By the example of commercial cokes, synthetic graphite and foam graphites, it has been shown that it is possible to regulate the reactivity and, respectively, thermal stability of carbon materials (CMs) in the reaction with CO₂ by an increase in the composition of a carbon material (CM) a fraction of graphite structures and by introduction of catalytic additives of 3d-metals (iron, cobalt, nickel), and also silicon or

aluminum. The action of additives is explained both by a change in CM graphitization degree and by a catalytic effect in the reaction.

Transmutation of Free Radical During Coal Pyrolysis Process

Ruimin Liu, Dexiang Zhang, Aiping Wu, Tieying Pan, Weiping Xia, East China University of Science and Technology; Shengchun Wang, Hebei United University, CHINA

Free radicals in coals and pyrolysis products are believed to play an important role in the mechanism of coal pyrolysis. The mode of stabilization of these radical may determine the type and the value of the product obtained. The shengli brown coal pyrolysis experiment were carried out at the horizontal tube furnace with N₂ as the carrier gas and the pyrolysis temperature ranging from 350 to 650°C over 1.5-30min. The effects of temperature and reaction time on the oil-gas yield and semi-coke conversion rate were investigated. Simultaneity, the quantitative information of the free radical from the semi-coke was provided by the Electron Paramagnetic Resonance (EPR).

In order to investigate the reaction mechanism during the pyrolysis process, the free radical concentration (N_g) of coal and semi-coke were tested by the EPR. The N_g of the shengli coal was 3.0346×10¹⁸/g. The N_g of the semi-coke was found to have the greatest dependence upon pyrolysis temperature. The N_g of semi-coke results show that the N_g increases with the reaction time and reaches a maximum value, and then decreases in the condition of same temperature. The timing of the maximum value appears shorter and shorter with the temperature increasing. In a constant temperature as 400°C, the N_g value increases from 7.4650×10¹⁸/g to 16.8092×10¹⁸/g when the reaction time 1.5min and 25min, and then decreases to 15.8525×10¹⁸/g on 30 min. The maximum value of the N_g reaches 35.1186×10¹⁸/g at 500°C and 20min reaction time. The oil-gas yield rises with the increasing of temperature and reaction time and reaches a maximum value 42.70% at 650°C and 30 min. Simultaneously, the semi-coke conversion rate gets the minimum value 67.41%.

It can be deduced that the increase of N_g was led by the broken of chemical key in coal molecule at first. And then the polycondensation of the free radical play an important role in the decreasing of the N_g.

The Efficient Energy – Assessment of Influence of Ash Content in Coal on Moisture Bonding

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From the point of view of energy production, moisture of coal is very important parameter which is influencing calorific value. The high content of water in coal decreases efficiency of combustion processes because part (20 – 25 %) of heat produced by combustion is used for evaporation of water. For the obtaining of effective energy it is necessary to know the behaviour of water in coal. For the study there were selected 2 samples from the Coal Mine Libous (Severoceske doly, a.s. Chomutov) and 1 sample from Germany, Coal Mines Mibrag (Rohrbraunkohle). The Mines Mibrag are extracting coals with calorific values of 9 – 11.5 MJ/kg containing 6.5 – 9 wt % of ash, moisture 48 – 53 % and sulphur concentration of 1.5 – 2%. The sample from the Mine Libous has moisture approximately of 30 – 32 %, content of ash 31%, calorific value 11.5 MJ/kg and concentration of sulphur 2.5 – 3%. The compared samples of coal have significantly different moisture. The determination of reasons of high moisture was focused on standard parameters which influence the bonding of water in coal and besides it on the research of hydrophobicity by measurements of the contact angle between water drop and coal surface.

Water in coal is bound at the surface of coal particles by adsorption (Surface moisture) or inside coal by capillary force (inherent moisture). Coal moisture depends on relative air humidity. Capillary coal moisture depends on the grain size distribution, petrographical composition and degree of coalification which is related to the content of carbon and oxygen. Sorption of water on coal can be dependent on hydrophobicity of coal. Hydrophobicity of coal decreases with the degree of coalification, total bound carbon and with increasing content of oxygen and amount of hydroxyl groups.

The hydrophobicity of coal was determined by the method of measurement of contact angle (CAM 200 apparatus). The sample of Mibrag coal has pronouncedly hydrophobic character. The measured value of contact angle was 130° while coal from Mine Libous has hydrophilic character – the value of contact angle ranged between 35° and 45°. The low content of ash in Mibrag coal is the cause of its high hydrophobicity. Macerals are hydrophobic. Clay minerals and other silicates are hydrophilic (Ruiz et al. 2008).

From these results it follows that content of ash in coal significantly influences bonding of water. The relatively higher absorbing capacity under unfavourable meteorological conditions will influence the calorific value which will decrease from 21.4 down to 9.4 MJ/kg in dry matter for the Mibrag coal. The decrease of calorific value for coal from the Mine Libous under similar conditions will be smaller – from 16.6 to 11.5 MJ/kg.

The Coal Resources of Vietnam and Its Current Coal Utilization Technologies

Nguyen Viet Quang Hung, Vietnam Academy of Science and Technology, VIETNAM; Masakatsu Nomura, Osaka University, JAPAN

In this report, the authors would like to introduce coal resources, some analytical results about coal samples, the current coal utilization technologies and cooperation about coal industry in Vietnam. The coal resources of Vietnam are distributed from North to South, however, mainly in the North, concentrated in Quang Ninh coal basin. Total coal reserves of Vietnam (published on January 1st, 2010) are about 49.8 billion tons. Now Vinacomin (Vietnam National Coal and Mineral Industries Holding Corporation Limited) mainly handles coal in Vietnam. The growth of coal yield of Vinacomin is high, from 27.5 million tons in 2004 year to 47.5 million tons in 2010 year (on average 12.1% increase /year).

Coal types of Vietnam according to the coal classification of Vinacomin are anthracite, subbituminous coal, peat coal, fat coal and brown coal. Note that fat coal is a type in the coal classification of Vinacomin, however, it is not in other coal classification of many authors in the world.

One of authors went to the Quang Ninh, Lang Son and Thai Nguyen provinces and cooperated with chiefs of these coal companies. In these places he collected 26 coal samples, after that the authors selected 3 coal samples to have sent to the Coal Testing Lab. in Japan. Beside this the authors referred to the data of the two coal samples at the Red River Delta coal basin from Petro Vietnam Journal. From these data, according to dry ash free basis we get the following elemental analyses after calculation:

1. Coal sample in Quang Ninh province: C% 96.46%, H% 1.33%, (anthracite). H/C ratio is 0.16. 2. Coal sample in Lang Son province: C% 73.4%, H% 4.2%, (brown coal). H/C ratio is 0.68. 3. Coal sample in Thai Nguyen province: C% 87.5%, H% 3.3%, (bituminous coal). H/C ratio is 0.45. 4. Coal sample in Hung Yen province: C% 70.37%, H% 7.02%, (brown coal). The atomic ratio of H/C is 0.98. 5. Coal sample in Thai Binh province: C% 70.93%, H% 5.85%, (brown coal). The atomic ratio of H/C is 1.19.

It is very interesting to note that S% of these five coal samples is ranging from 0.31% to 1.4% with exception of 5.9%. Ash% of these five coal samples is ranging from 2.2% to 17.9% via 5.2%. CaO is a major component for ash of two brown coals in Hung Yen and Thai Binh provinces.

The authors have concentrated their attention to the result of No.3 and based on the coal classification of the reference of A. Williams et al, they have found that the coal sample collected in Thai Nguyen province is bituminous coal (this bituminous coal has been not mentioned so far in all documents in Vietnam). So the authors suggest that it seems to be adequate to add bituminous coal to coal types of Vietnam and to evaluate reserve of this bituminous coal type in addition to planning for the sensible use of this coal. Results of this analysis and this finding bring about reconsideration of the coal classification in Vietnam and will raise somewhat influence on exporting, importing and using coal in Vietnam.

In Vietnam, coal is used in some fields: thermal power plants, cement production, fertilizer synthesis and chemical industries, paper industry, metallurgical industry, construction materials, batteries and cell industry, household, etc. Coal plays an important role in energy balance. Demand for electricity of Vietnam is expanding rapidly due to the current growth of industries, in 2010 about 98terawatt/h while in 2004 about 46.2terawatt/h. Because the hydroelectric resources potential is almost finished in Vietnam, now the Vietnamese Government strengthens to use other energy sources such as thermal power, wind power, solar power, nuclear power, biogas power, etc. Vietnam has been building many thermal power plants. The authors also introduce some results of recent successful cooperation.

Effect of the Burning Profile on the Reactivity of Lignite

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This study investigates the effects of the characteristic temperatures of the burning profile on the reactivity of 15 lignite samples originating from different areas of Turkey. Nonisothermal thermogravimetry has been used to determine the combustion reactivity of the samples. The combustion activation energies were calculated by the Coats Redfern method from their TG data. It was observed that the characteristics of the temperatures of the burning profile had an important effect on the activation energy of the lignite samples and that there are definite correlations between them.

Influence of Binderless Briquetting Process with Dried Low Rank Coal Having the Various H₂O Contents on the Physical and Chemical Properties of Coal

Changsik Choi, Jung Hee Jang, Gi Bo Han, Yongseung Yun, Institute for Advanced Engineering; Jaehyeon Park, Dowon Shun, Sihyun Lee, Korea Institute of Energy Research, KOREA

In this study, the dried low rank coal (LRC) was briquetted and then the influence of briquetting process on the physical and chemical properties of dried LRC was investigated by the characterization with various analysis methods. In briquetting process, the operation conditions such as feeding rate, briquetting speed and briquetting pressure of briquetting machine and the H₂O content of dried LRC was controlled as a factor. After the briquetting process, the textural properties such as BET

surface area, thermal characteristics such as ignition temperature of dried LRC were varied by surface morphologies. In TGA results, the thermal oxidation was relieved and the thermal stability was improved due to the decrease of the surface area and the removal of the pore structure after briquetting process. And then it was observed that the ignition temperature decreased by the briquetting process.

Influence of Surface Treatment on Dispersion and Solubility of Coal in Solvent and Ionic Liquid

Gi Bo Han, Jung Hee Jang, Changsik Choi, Yongseung Yun, Institute for Advanced Engineering; Tae Jin Lee, No-Kuk Park, Yeungnam University, KOREA

The new process for the supply to meet the demand of liquid fuels should be developed because the demand of the liquid fuel dramatically increases; however, the oil reserves and its supply are restrictive and its price steeply increases, recently. Therefore, the various direct and indirect liquefaction processes using the various resources like coal, biomass with the exception of oil for the renewable energy production have been investigated. Nowadays, the direct coal liquefaction process to produce the transportation fuels has been interested because the coal has much more reserves and much cheaper than the oil. It was estimated that the chemical and physical properties of coal surface have an influence on reaction characteristics of the coal hydrogenation and cracking in the direct coal liquefaction for the production of the transportation fuels. In this study, the surface treatment of coal was conducted by the various drying methods, and then the chemical and physical properties of coals were characterized by the various analysis methods. Also, it was investigated the effect of the various and different physic-chemical properties of coal on the characteristics of coal dissolution in the various solvents of the direct liquefaction process.