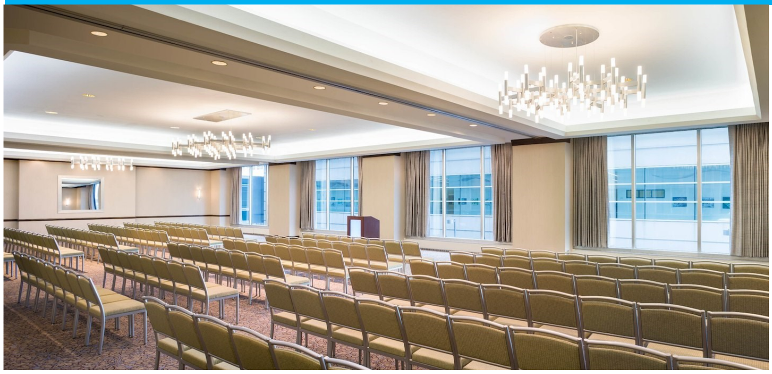
Thirty-Sixth Annual
INTERNATIONAL PITTSBURGH
COAL CONFERENCE

University of Pittsburgh · Swanson School of Engineering

ABSTRACTS BOOKLET

Clean Coal-based Energy/Fuels and the Environment

September 3 - 6, 2019
Westin Convention Center Hotel
Pittsburgh, PA, USA



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On behalf of the Thirty-Sixth Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation and gratitude to Ms. Kristen Harper for her meticulous leadership and control of the entire operation of the conference and to Mr. Husain Ashkanani, Mr. Rui Wang and Ms. Sudesna Banerjee for their invaluable assistance in preparing this Abstracts Booklet.

Thank you,

Badie I. Morsi

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

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SESSION 1
CLEAN COAL AND GAS TO FUELS I: LIQUEFACTION AND FISCHER-TROPSCH
John Duddy and Diane Revay Madden

1.1 Low GHG Emitting Fisher Tropsch Process in Supercritical CO_2 with Integrated Recycle

Kanchan Mondal, Southern Illinois University, USA.

Syngas production from coal results in the formation of substantial amounts of CO2. The produced syngas does not have the required stoichiometric ration of H2:CO (=2) for FTS and often requires upgradation via WGS reaction which in turn produces more CO2. Additional CO2 is generated in the FTS process, especially if the catalyst is Fe-based. Co based catalysts somewhat reduce the CO2 production in the syngas, but the costs are nearly three orders higher and they are unable to operate efficiently coal derived syngas. We present a process that can be used for the production of liquid fuels from coal-based syngas (H2:CO ≤ 1) over Fe-based catalysts while completely suppressing the formation of CO2 in the FTS process. The carbon efficiency in in CTL is about 16.9 % using iron-based catalysts while the presented technology has shown that this efficiency can be improved to 51.1 %. This enhanced reduction of net CO2 emission is achieved not just by the complete suppression of CO2 production but also conversion (~10%) of some of the CO2 produced during the gasification and upgradation stages to liquid hydrocarbons. In the process,CO2 (produced in the upstream processes) is co-fed such that the CO2:syngas ratio in the reactor is above 3.33:1 and conducting the FTS at conditions above the critical pressures and temperatures of CO2. The use of supercritical (ScCO2)/compressed phase enhances the diffusion of the gases through the solvent (CO2) as compared to slurry reactors and of the order expected in gas phase reactors. The use of ScCO2/compressed CO2 enhances the heat capacity, conductivity and solvent power of the fluid. The co-feeding of CO2 eliminates the need for CO2 capture upstream of the FTS reactor which will aid in the cost competitiveness. The effects of operating and feed conditions will be presented. The parameters that were evaluated were CO2:Syngas ratio, H2:CO ratio in syngas, feed rate, catalyst loading, temperatures and pressures. A lower limit for the CO2:Syngas ratio was determined for maximized pure hydrocarbon production. A minimum 70 % liquids selectivity was observed in all cases. Conversions as high as 98 % were observed. Even at these high conversions, methane selectivities were as low as 0.9 %. Negative CO2 selectivities was observed in nearly all cases under supercritical conditions. The product stream showed a decrease of 10 % in the CO2 mass flow rate. Thus, both the primary GHGs were drastically subdued while attaining high conversions and no loss of liquid throughput. It was observed that the life of the catalyst was more than doubled when ScCO2 was used at the same pressures and even more when compared to conventional conditions. The increase in the lifetime of the catalyst further reduces the lifecycle CO2 emissions since the amount of catalyst processing required per unit fuel produced is lowered. The ScCO2 – FTS process also takes advantage of the strong solvent yet tunable power of ScCO2 and allows for pressure tunable fractionation of the products. We will present the product distribution in four fractions obtained by pressure tunable fractionation. Furthermore, we will also present the performance and product distribution resulting from the recycling of the gaseous exit stream. Recycling the product gas in ScCO2 FTS provides two unique advantages. (A) recycle helps in improving the throughput (reduced reactor size). (B)Advantages of ScCO2FTS are further enhanced by the recycle of HC gases (along with the unreacted feed) since HCs like hexane and pentane become supercritical. The net result observed were higher selectivity towards liquids, lowered selectivity towards methane and improved carbon efficiency in coal and biomass to liquid fuels process than the original process. Studies conducted on the recycle of product gas have shown that an increase in conversion for the same reactor volume, a decrease in reactor volume for the same conversion, an increase in liquid fuels yield and CO2 converted for the same reactor volume, improved liquid selectivity, further enhancement in catalyst life and improved pressure tunable fractionation efficiencies (higher than theoretical estimations). For example, theoretically, recycling does not affect the liquid selectivity. We observed a 25 and 30 % increase in liquid selectivity due to recycle on Fe-Co- Zn-K and Fe-Zn-K catalysts, respectively. Similarly, the theoretical expectation of the reduction in volume was around 2.5 times when a recycle ratio of 5 is employed when maintaining the same conversion. However, the observed reduction in volume required was around 3.2 times while the conversion was further improved by 4.5 %.

1.2 Fischer Tropsch Synthesis Like Process on Commercially Available O-Functionalized CNTS

Kanchan Mondal, Saikat Talapatra, Southern Illinois University; Mauricio Terrones, Pennsylvania State University; Praveen Alagiri, Southern Illinois University, USA.

Worldwide energy independence is reliant on the ability to leverage locally available resources for fuel production. Production of chemicals including transportation fuels may be realized though the catalytic transformation of gasification products (syngas) from carbonaceous materials. The basis of the production of gasoline and diesel-like fuels is the Fischer Tropsch Synthesis (FTS) process: A catalyzed chemical reaction that converts a mixture of carbon monoxide (CO) and hydrogen (H2) into long chain hydrocarbons. Until now, it has been argued that only transition metal catalysts (usually Co or Fe) are active toward the CO hydrogenation and subsequent chain growth in the presence of hydrogen. We have recently demonstrated that metal-free, carbon nanotube (CNT) surfaces are also capable of hydro-deoxygenating CO and producing long chain hydrocarbons similar to that obtained through the FTS but with orders of magnitude higher conversion efficiencies than the present state-of-the-art FTS catalysts. Our initial studies have identified C-O functional groups as the active sites for the enhanced catalytic activity which were confirmed by our quantum Density Functional Theory (DFT) calculations. The DFT calculations have shown that the kinetically and thermodynamically feasible route for CO insertion and hydro-deoxygenation are different from that on transition metal catalysts. In this paper we evaluate three different O functionalization of multiwalled nanotubes; namely C=O, COOH and C-O; on the activity for CO hydro-deoxygenation and chain growth. Both lab manipulated CNTs as well as commercially obtained O-functionalized CNTs were used. Experiments on a continuous flow tubular reactor with these metal-free CNTs have been carried out and the products have been analyzed. Reactor tests revealed that the hydrogen pre-treatment reduced the activity of the catalysts to negligible levels. Without the pretreatment, the activity for CO conversion as found to be greater than 110 µmol CO/g CNT/s. Analyses show that CO hydro-deoxygenation occurred at the C-O/O-H functional groups. It was found that while the products were similar to FT products, differences in selectivities were observed which, in turn, were a result of a different catalytic mechanism. The product distribution was also found to be different for the three oxygen functionalizations. These findings now open a new paradigm for CNT-based hydrogenation catalysts and constitute a defining point for obtaining clean, earth abundant, alternative fuels through the use of efficient, renewable and commercially available catalyst.

1.3 Enhanced Direct Coal Liquefaction with CO2 Capture

John Duddy, HTI, USA.

Coal is hydrogen deficient with a H/C atomic ratio < 1, typically about 0.8. Liquid transportation fuels, gasoline and diesel have a hydrogen to carbon ratio of 1.8-1.9. Conversion of coal to liquids requires the adjustment of the H/C ratio. There are 2 primary technologies to do this. One route is so-called indirect coal liquefaction. In indirect coal liquefaction the coal is first gasified with oxygen and steam to produce syngas, a mixture of CO and H_2. The syngas is further processed to adjust the H_2:CO ratio and remove impurities. The purified syngas is the process in FT synthesis, which catalytically hydrogenates the CO and forms liquids that are then further refined to produce fuels. The other route is direct coal liquefaction, which converts the coal to oil directly. Usually in a coal-oil slurry using process derived oil to make the slurry, with a hydrogenation catalyst and hydrogen at elevated temperature (400-450 °C) and pressure (150-200 bar). The raw liquids are further refined just like the indirect route to produce high quality gasoline and diesel fuels. It follows then, that direct coal liquefaction requires a source of hydrogen. In the US a low-cost source of hydrogen is available via steam reforming of cheap and abundant natural gas. However, this production of hydrogen results is a very significant co-production of CO_2. This presentation will show the CO_2 production from direct coal liquefaction and evaluate technology options and economics for capture of CO_2, and compare the CO_2 emission profile to conventional and heavy oil petroleum refineries in North America.

1.4 Preparation Characterization and Liquefaction Properties of Fe_7S_8

Ruo-qing Wang, Xiao-hong Li, Hai-jie Li, Jie Feng, Wen-ying Li, Taiyuan University of Technology, CHINA.

Direct coal liquefaction(DCL) technology has been invented by German since the beginning of the 20th century. DCL is a process of converting coal into oil, which is actually a hydrogenation process. Lignite is a low-rank coal, which is easy to be liquefied because there are much carboxyl groups, oxygen bridges, carbonyl and methylene groups in the structural units of lignite. This paper chosen HulunBuir lignite as raw material and Fe7S8 as catalyst for the liquefaction experiment. Fe7S8 of hexagonal structure (PDF-25-0411) and monoclinal structure (PDF-52-1516) were respectively prepared by solubility heat method and novel flux method. Phase identification was carried out by XRD and particle size was further calculated by Scherrer Formula. XRD patterns shows that Fe7S8 of hexagonal and monoclinal structure were synthesized successfully and particle size were in the range of 21-26nm and 48-52nm. Considering the preparation temperature (240°C) of Fe7S8 with hexagonal structure is lower than the liquefaction temperature (450°C), TG-DTA was performed to identify the structural transformation of Fe7S8. DTA showed an obvious exothermic process at about 430°C, which indicated the phase change occurred. XRD pattern of Fe7S8 sample after TG-DTA showed the conversion from Fe7S8 to Fe1-xS(PDF-29-0726). So the crystal structure change in direct liquefaction needs to be further studied. The results of lignite liquefaction with different Fe7S8 as catalysts showed that Fe7S8 of hexagonal structure has better liquefaction activity than monoclinal structure. But we cannot confirm the advantages of hexagonal structure because its smaller grain size may play a bigger role in liquefaction. Therefore, we further prepared more Fe7S8 samples to identify the effect of crystal structure and particle size, after which we continued to explore the mechanism of Fe7S8 in liquefaction. There are different crystal structures in Fe7S8, meaning the different arrangement of atoms and number of vacancies exposed in a unit cell, which may lead different liquefaction activity. So the following study emphasis is the role of vacancy in different crystal structure in DCL.

1.5 The Effects of Hydrothermal Treatment on Structures and Liquefaction Behaviors of Lignite

Huan Li, Shiyong Wu, Youqing Wu, Sheng Huang, Jinsheng Gao, East China University of Science and Technology, CHINA.

The effects of hydrothermal treatment on structures and liquefaction behaviors of lignite were studied in this paper. The lignite was pretreated at lower temperatures (70℃-280℃) under N_2 atmosphere with (and without) water, and the elemental compositions and acidic functional group contents of pretreated lignite were determined. Then, the lignite after hydrothermal treatment was liquefied at 430℃ under H_2 atmosphere. Compared to pretreated lignite without water, the C content of water-treated lignite was lower, and its H and O contents were higher in the temperature range of 70℃-250℃, mainly due to the formation of carboxyl groups and phenolic hydroxyl groups in water-treated lignite. Through hydrothermal treatment, the C-O/C=O in lignite decreased with the increase of temperature, suggesting that C-O was decomposed easily. Besides, the water played a weak role in hydrogen donating, and the conversions and oil yields of water-treated lignite were higher than those of pretreated lignite without water. Therefore, the structures of lignite were changed by hydrothermal treatment, and the hydrothermal treatment at lower temperatures (130℃-220℃) was in favor of lignite liquefaction.

SESSION 2
GASIFICATION TECHNOLOGIES I
Gary Siegel And Johan Van Dyk

2.1 Overview of DOE Coal Gasification R&D

Jai-woh Kim, Dave Lyons, Regis Conrad, US Department of Energy, USA.

The Gasification Systems Program, conducted under the U.S. Department of Energy’s Office of Fossil Energy (FE) and National Energy Technology Laboratory (NETL), have developed advanced technologies that reduce the cost of coal gasification enabling high efficiency and excellence environmental performance of coal syngas-based power production.

Due to low prices of natural gas and oil and high capital investments required for large conventional coal gasification plants, the FE Gasification Systems Program is focusing on new advanced small-scale, modular gasification-based coal conversion for the reduction of cost of electricity with improvement of efficiency while minimizing the cost and energy penalty. The research and development (R&D) activities have made significant progress in the area of dry solids pump coal feed for high pressure, oxygen separation, reactor engineering design, product & site-optimized technologies and key technologies systems integration.

This talk will highlight a broad overview and progress that DOE’s Gasification Systems Program has made on small-scale, modular gasification systems and cost reduction of each component of the overall gasification system along with a detailed discussion of future coal conversion technology advances.

2.2 Innovative, Modular, and Flexible Coal-based Energy Systems

K. David Lyons, National Energy Technology Laboratory, USA.

The U.S. Department of Energy’s National Energy Technology Laboratory (DOE/NETL) Gasification Program is developing small-scale, low-cost, and efficient coal gasification-based energy systems. Modular gasification could produce clean syngas from coal for flexible production of power (e.g., in a fuel cell, combustion turbine, or heat engine), and for production of high value products such as fuels and chemicals. Innovative small gasifiers enabling highly efficient and competitive power production in the range of 1-5 MW could be configured in modular systems incorporating advanced technologies. NETL is envisioning the 1-5 MW-scale components and systems will be readily scalable to one order of magnitude larger, increasing possibilities for deploying these energy systems across a broad market. Research and development in this area is underway at NETL, emphasizing principles of process and/or reaction intensification, innovative unit operation design with superior performance at smaller scales, and other enabling technologies. Accelerated technological development is possible using NETL’s sophisticated modeling and simulation capabilities; advanced materials and fabrication methods; and by leveraging NETL’s partnerships with industry, academia, and other national laboratories.

This presentation will review DOE’s Gasification Program showing how this technological development will serve as the foundation for future low-cost coal-based energy systems that will enable new applications for coal in the United States.

2.3 Advanced Syngas Cleanup for Radically Engineered Modular Systems

Atish Kataria, RTI International, USA.

The focus of the Small-Scale Modularization of Gasification Technology Components for Radically Engineered Modular Systems funding opportunity announcement (FOA) is the development of emerging gasification technologies that can be scaled down to modularization using the REMS concept to advance DOE’s program goals of developing advanced energy-conversion systems designed to enable efficient, low-cost, near-zero emission energy from existing and new fossil fuel power plants. Advances in gasification technology are an important facet of unlocking the full potential of domestic coal resources, which both improve U.S. economic competitiveness and contribute to the protection of the global environment.

RTI has developed its Warm Syngas Desulfurization Process (WDP) technology that is based on dual transport reactor loops and a robust attrition-resistant, and regenerable sorbent that is effective at syngas temperatures as high as 600°C. High temperature desulfurization enables advantageous integration with the gasifier and downstream processes since the syngas is delivered to the downstream processes at higher temperatures which improves overall thermal efficiencies by up to 10%. The transport-based design for WDP results in a small-footprint system that is economical because it is constructed primarily of pipe, has few moving parts, and has very short residence time requirements. The WDP technology has been successfully demonstrated at pre-commercial scale on 50-MWe slipstream of coal/petcoke-based syngas from the gasifier at Tampa Electric Company’s Polk Power Station. During these tests, sulfur removal exceeded 99.8% for both hydrogen sulfide (H2S) and carbonyl sulfide (COS).

The efficiency improvement upon using the WDP technology is independent of scale and will also occur for a REMS-based plant and generate additional overall life-cycle greenhouse gas reductions. Also, the key components of WDP that enhance its cost competitiveness for such large-scale systems are also ideally suited to design standardization, mass manufacturing, and the application of advanced manufacturing techniques that should enable even greater relative cost reductions for smaller scale processes envisioned for REMS-based plants. At the envisioned small scale of REMS-based plants (1 to 5 MW), especially for low-sulfur coals, fixed-bed processes can also become viable alternatives as they have many of the same simplified design aspects as the WDP transport-bed process. Many U.S. coals, particularly western coals that represent over half of domestic coal production, have considerably lower total sulfur levels (600 to 3,000 ppmv) in their syngas, and such low-sulfur coals will represent an important potential market for REMS plants.

This presentation will provide an overview of the status of the development of modular sorbent-based warm syngas cleanup designs that will enable 1- to 5-MW REMS-based plants to be cost-competitive with large state-of-the-art commercial plants utilizing all of our abundant domestic coal reserves. Successfully achieving this overall objective is incumbent on achieving several more focused sub-objectives, which include parametric testing of sorbent desulfurization performance at typical operating conditions for low-sulfur syngas, development of hydrodynamic data for the design of a fluid-bed regenerator for small-scale application, development of a fixed-bed desulfurization process design and a fixed-bed desulfurization sorbent that has similar chemistry and desulfurization performance as our current WDP sorbent, and techno-economic analyses (TEAs) of overall REMS plants for combined heat and power or polygonation using coal gasification.

2.4 R-GAS Gasification Technology and Demonstration Project Status

Eric Z. Zhou, Gas Technology Institute, USA.

Developed based on the advanced rocket engine propulsion combustion technologies, GTI’s R-GAS™ technology offers a pathway for direct gasification of a variety of coals, including high ash content, high ash-fusion temperature coals, as well as petroleum coke. Its efficient, compact, high-performance design eliminates the need for feedstock blending and/or fluxant addition, as is required with other existing commercial technologies, and therefore provides a cost-competitive solution for the clean utilization of challenging coals.

The R-GAS system is a dry-feed entrained flow coal gasification technology that utilizes proprietary feed injector elements and ultra-dense phase coal feeding system to establish a plug flow pattern in the gasifier through rapid and efficient mixing, allowing the gasification reactions to occur at high temperature. The unique features of the R-GAS gasifier reduce the reaction residence time, providing peak performance in a compact reactor design. The R-GAS gasifier pressure vessel is protected by a water-cooled liner designed for high heat flux, keeping the metal at safe temperatures during operations while maintaining the high gasification temperatures in the reaction zone for effective conversion and the liner-exit temperatures above the ash fusion temperature for proper slagging operations. The raw syngas from the liner-exit is partially quenched using the specifically configured water spray nozzles allows for both dry and wet removal/recovery of fine ash. R-GAS technology has been successfully operated at GTI's pilot-scale (18 tons per day) facility in Des Plaines, IL on sub-bituminous coal, bituminous coal, high ash fusion temperature anthracite coal, and petroleum coke - all with excellent test results.

GTI and Yangquan Coal Industry Group, a Global Fortune 500 company, have established a joint development partnership for an 800 MTPD Industrial Demonstration Project to demonstrate the commercial readiness of the R-GAS gasification process in China. The installation is located at the largest coal-to-chemicals plant in Shanxi Province and will be integrated with the existing plant system. The project follows up the successful long-duration testing of high ash-fusion temperature coal using GTI's R-GAS pilot-scale facility. Over 300 hours of pilot plant operation with the high ash content, high ash-fusion temperature coals from Yangquan's coal mines, the R-GAS process had demonstrated successful gasifier operations with carbon conversion up to 99% and direct utilization of feed stocks with ash fusion temperatures exceeding 1,600°C and ash content exceeding 28wt%. The success of the pilot plant studies provided a solid basis for a commercial-scale R-GAS unit.

After completion of the process design package, HAZOP analysis and detailed engineering, the project partners of the 800 MTPD R-GAS Industrial Demonstration Project are presently wrapping up the construction activities, targeting a mechanical completion in serval months from now and commissioning scheduled to begin by the end of 2019. The demonstration unit expects to achieve carbon conversion and cold gas efficiency (CGE) up to 99.9% and 80%, respectively. Successful demonstration of the R-GAS gasification technology will further prove its commercial viability as a new industrial solution for the efficient and clean utilization of low-quality coals, in particular of the high ash content, high ash-fusion temperature coals, in China and around the world.

2.5 The Development of ECUST OMB Coal-Water Slurry Gasification Technology with Radiant Syngas Cooler

Qinghua Guo, Jianliang Xu, Yan Gong, Guangsuo Yu, East China University of Science and Technology, CHINA.

The Opposed Multi-Burner (OMB) coal-water slurry gasification technology adopts an entrained-flow gasifier to produce syngas (CO+H2) under high temperature and pressure operating conditions. Up to now, the OMB coal-water slurry gasification technology has been licensed on 57 projects for a total of 158 gasifiers. The design coal capacity is ranging from 750 to 4000 TPD for single gasifier and pressure ranging from 1.5 MPa(G) to 6.5 MPa(G). There are 74 gasifiers on 28 different projects currently running smoothly in China with the largest one having a 3000 t/d coal capacity. The OMB coal-water slurry gasification technology with Radiant Syngas Cooler (RSC) is developed based on current entrained-flow gasifier for heat recovery from the high temperature raw syngas by membrane wall of the RSC. The demonstration plant with this RSC combination gasification technology with a capacity of 2000 t/d and operating pressure 6.5 MPa(G) is built in Yankuang Yulin Co. Ltd. The high temperature raw syngas was cooling down from ~1340 ℃ to ~800℃ by the RSC. Correspondingly, the saturated steam production by the RSC is ~100 t/h with a temperature of 319℃ and a pressure of 11.1 MPa(G). Then the syngas flows into the quench chamber subsequently, which is same as the traditional OMB quenching process as well as the downstream process. This project is now under construction with an expectation of commissioning by the end of year 2019.

SESSION 3
POWER PLANTS I
Ting Wang and Nick Siefert

3.1 Supercritical Carbon Dioxide (sCO_2) Based Power Cycles in Fossil Fueled Power Plants

Richard Dennis, National Energy Technology Laboratory (NETL), USA.

The US Department of Energy is investing in the development of power cycles based on supercritical carbon dioxide (sCO2) as the working fluid. Power plants based on these cycles have the potential for a lower COE with better efficiency in many heat source applications including fossil fuels, concentrated solar power, nuclear energy and waste heat recovery. The DOE is investing in all of these applications. The DOE Office of Fossil Energy manages R&D projects supporting the Recompression Brayton cycle, the Allam cycle with carbon capture and cycles optimized for waste heat recovery. This presentation will present an overview of research activity in sCO2 based power cycles in the DOE Office of Fossil Energy.

The presentation will discuss two primary sCO_2 cycles: the recompression Brayton cycle and the Allam Cycle. The RCB cycle uses SCO2 as the working fluid and can be seen to replace steam-based Rankin cycles in thermally heated applications like coal combustors, concentrated solar power and nuclear energy. The Allam cycle is a semi-closed cycle that is directly fired with pure oxygen and gaseous carbon-based fuels producing high turbine inlet temperatures, the working fluid is SCO2. Both cycles offer a line of sight to lower cost and higher efficiency applications. The Allam cycle is designed for 95 % CO2 capture. The benefits and technical challenges of these cycles will be discussed. A relevant project portfolio will be presented including the world's largest and most advanced demonstration of a Recompression Brayton cycle.

(Presentation # 3.1 is 40 minutes long)

3.2 Legal Update on Hydrologic Connection Cases Under the Clean Water Act,

Hollister A. Hill, at Troutman Sanders, USA.

This panel/paper will review the case law on hydrologically connected groundwater cases, including the cases leading to the U.S. Supreme Court taking one of the cases for decision. Several of these cases involve ash ponds and the in place closure of those ash ponds. I will discuss the history of each case, where the current issue stands, some of the politics behind the cases, and what the Supreme Court might decide. In addition, I will review and discuss EPA's recent Interpretive Statement (April 2019) on this issue. This panel/paper is different because it centers on a legal issue, but it is very relevant to coal ash and ash pond closures. Also, a technical audience often enjoys an update on legal cases involving their technical issues since they are not familiar with the legal side but can be educated on the essential take-aways in a brief, straightforward presentation.

3.3 Comparison of an Integrated Mild/Partial Gasification Combined (IMPGC) Cycle with Other Power Cycles

Henry A. Long, III; Ting Wang; University of New Orleans, USA.

Designed as a potential retrofit option for existing Rankine cycle plants, the Integrated Mild/Partial Gasification Combined (IMPGC) Cycle is an attractive concept in cycle design that will greatly increase the efficiency of coal-based power plants. Coal is traditionally seen in a negative light due to its high sulfur and ash content and its status as a fossil fuel. Nonetheless, coal is a vital source of energy for many countries, so it becomes necessary to find a way to utilize coal in a cleaner and more efficient manner. The idea of IMPGC was inspired by a warm gas desulfurization scheme developed by Research Triangle Institute (RTI), which has been named the High-Temperature Desulfurization Process (HTDP). Compared to the Integrated Gasification Combined Cycle (IGCC), IMPGC uses mild gasification to purposefully leave most of the volatile matters within the feedstock intact (hence, yielding more chemical energy) compared to full gasification and uses partial gasification to leave some of the remaining char un-gasified compared to complete gasification. The larger hydrocarbons left over from the mild gasification process grant the resulting syngas a higher volumetric heating value, leading greater power output from the GT and therefore higher efficiency. The leftover char due to the lower gasification temperature can then be burned in a conventional boiler to boost the steam output of the bottom cycle, preventing a potential loss of efficiency from underutilized exergy, resulting in an overall thermal efficiency of 47.9% (LHV).

This paper will focus on developing the baseline IMPGC system and then compare it to a number of other common fossil power systems, including IGCC, a subcritical Rankine cycle, an ultra-supercritical (USC) Rankine cycle, and a natural gas combined cycle (NGCC). The results show that, compared to other common coal power cycles, this is competitive with ultra-supercritical Rankine cycles (44.37%), around seven (7) points better than traditional IGCC (40.87%), and around nine (9) points better than traditional sub-critical Rankine cycles (38.99%). Only NGCC is superior to IMPGC in terms of efficiency (55.57%). In addition, on a per-unit-net-power basis, IMPGC has the lowest emissions of all coal plants in nearly all categories, provided SCR is not used in the Rankine cycles. Overall, IMPGC is an innovative new idea that has the potential to greatly increase the viability of using coal for power, and numerous optimizations can still be made at this juncture, with the eventual goal of achieving 50% (LHV) efficiency or higher.

SESSION 4
COAL SCIENCE I
Leslie Ruppert and Atsushi Ishihara

4.1 Separation Mechanism of Fine Coal Particles in Vibrated Fluidized Bed

Liang Dong, Xuchen Fan, Yuemin Zhao, China University of Mining and Technology, CHINA.

Coal as the dominant energy in our country. With the improvement of mechanization level, more and more coal has been mined, especially -6 mm fine particles. So vibrated fluidized bed is the more efficient way for fine coal separation. This paper is based on the feed particles (-6mm) in vibrated fluidized bed, using bed pressure testing system and high-speed camera, to study the effects of feeding position, medium properties and operating conditions on feed particles behavior in the fluidized bed. The prediction model of particle retention position with different condition was established according to the experiment results. The optimal results using the prediction model showed that ash content of concentrates decreased to 10.33% from 33.56 % and probable error value E was 0.16g/cm3, which indicated that prediction model is efficient to improve fine coal beneficiation performance.

4.2 Fluidization Characteristics and Separation Performance of an Air Dense Medium Fluidized Bed for Coal Cleaning Based on Secondary Air Distribution Layer

Jingfeng He, Yuemin Zhao, China University of Mining and Technology, CHINA.

Air Dense Medium Fluidized Bed (ADMFB) separation provides an alternative approach for coal cleaning in the water-deficient but coal-rich counties and areas via desulfurization and ash reduction. Hydrodynamic stability within the ADMFB significantly influences the coal cleaning efficiency. Therefore, the secondary air distribution layer located the bed bottom was introduced to improve the air distribution stability of ADMFB, which facilitated its hydrodynamic stability. With 0.074-0.3 mm magnetite powder as fundamental dense medium, the apparent fluidization characteristics of the fluidized bed were investigated with the use of various-sized quartz sand as the filling of secondary air distribution layer. The results of fluidization tests showed that the optimum operational fluidization numbers (ratio of operational gas velocity and minimum fluidized gas velocity) were 1.6, 1.7, and 1.5 for achieving the stability of the bed density fluctuations with various-sized quartz sand of 0-0.15, 0.15-0.3 and 0.3-0.5 mm as the filling of secondary air distribution layer, respectively. The coarse-sized lignite with size fractions of 10-15 and 15-20 mm were used as the feed material for ADMFB. The separation efficiency of lignite was investigated through the orthogonal separation experiments based on the variables of size fractions of quartz sand, static bed height, fluidization number, and the height of the secondary air distribution layer. The results indicated that the appropriate size fractions of quartz sand were 0-0.15 and 0.15-0.3 mm for the efficient separation of 10-15 mm and 15-20 mm lignite. Under the conditions, the ash segregation degree reached the maximum of 0.70 and 0.78, respectively. The ash contents of 10-15 mm and 15-20 mm lignite were decreased from 15.32% and 14.35% to 8.25% and 9.49% with the clean coal yields of 28.26% and 50.57%, respectively. This work aims to provide fundamental laboratory-scale results for the dry-based cleaning of low-rank coal using ADMFB in industry.

4.3 Strategies on Coking Coal Utilization: A Key to Sustainable Development in Jharia Coalfield, India

Ashok K. Singh, Pradeep K. Singh, CSIR-CIMFR, INDIA.

Coal mining in Jharia Coalfield started in 1893, initially for supply of coal to steam engines but gradually it gained prime importance as coking coal producing coalfield for Indian steel plants. In current days also it retains its status as main repository of coking coal in India and catering the needs of Indian steel industry. Since mid-twentieth century much attention was not given on upgrading the required infrastructures in this coalfield. A thorough study was made on this coalfield to revise and update the strategic planning of this coalfield to enhance its quality coal production through upgradation of infrastructure.

Yield of steel-grade coal cleans at commercially acceptable ash value (17±0.5%) decreases significantly from >50% for upper seam-coals, to 12-30% for lower seam-coals, and that too with deterioration of coking qualities. Further, cleans prepared at desired ash levels, generally have lower reactive macerals for yielding good cokes, possibly due to presence of Near Gravity Materials (NGM). Further, amount of NGM increases from eastern to western parts of the basin, making washing of coals even more challenging.

Through simulation and pilot-plant experiments, following probable alternatives for beneficiation of Jharia coals have been proposed: a) Multi-stage beneficiation for the coals of east / central Jharia, having ash content about 35%, to four saleable products for Steel, Foundry, PF and FBC Power Plants, b) Multi-stream beneficiation for the coals in western part, having worse washability characteristics, to three saleable products suitable for industries like Steel, PF and FBC Power Plants, c) Selective mining, d) Fine coal treatment.

4.4 Operation Performance of FINEX® Process on the Different Reducing Agents

Jae Dong Kim, Jin Ho Ryu, Woo Il Park, Do Hyung Kim, Min Young Cho, POSCO Technical Research Lab, SOUTH KOREA.

The alternative iron-making process has been developed for the environmental issues that are fine dust and CO2 emission from sinter, coke manufacturing plant and blast furnace. The FINEX® has been scaled up from 0.6MTPA to 2.0MTPA and is currently in normal operation. Briquette coal and lump coal are representative reducing agents in smelting reduction iron-making process. To achieve the stable operation and high efficiency, the FINEX® process requires the proper strength of reducing agents. In this study, the strength of reduction agents that are briquette coal and lump coal was investigated by the cold strength such as compressive strength, shatter strength, drum index and high temperature strength respectively. And then, an analysis of the operation performance was carried out at #2FINEX, Pohang works when the different reducing agents were used. Briquette coal is higher than lump coal as respects of not only cold strength but also high temperature strength. When lump coal was used in place of briquette coal, fuel rate increased by the degradation of lump coal as a result. It indicated that the strength of reducing agents is considerable factor to implement stable performance and briquette coal has an advantage in efficient operation.

4.5 Influence of Electrochemical Action During Electroflotation on Flotability of Shenmu Coal Macerals

Anning Zhou, Wei Zhao, Xian University of Science and Technology, CHINA.

The minor difference in flotability among coal macerals is an important factor that restricts their flotation separation. It is an effective way to improve the flotation separation through proper surface treatment for changing differences in flotability of macerals. This paper focuses on Shenmu low metamorphic bituminous coal whose surface structure was adjusted by electrochemical action during electroflotation to improve the difference in flotability among macerals. The influence of electrochemical action on their surface structure was investigated. The changes of wettability and surface potential of coal macerals were researched. And the effect of separation and enrichment of electroflotation was evaluated. The results show that the electrochemical action result in electrochemical oxidation/reduction effect on surface functional groups of the macerals, especially surface oxygen functional groups as -OH and –COOH etc. during electroflotation. While, the surface wettability and potential of macerals are also changed, and difference in changes is also observed in the vitrinite and inertinite. The enrichment rate can be increased by up to 35% in vitrinite and 20% in inertinite respectively after electroflotation.

SESSION 5
VALUE-ADDED PRODUCTS FROM COAL I: BUILDING MATERIALS
Chunshan Song and Haim Cohen

5.1 Carbon Fiber from Coal Tar Pitch

Matthew Weisenberger, University of Kentucky Center for Applied Energy Research, USA.

It is largely a misnomer to say that carbon fiber is spun. It is, rather, produced by the carbonization of a spun precursor fiber. Something like 95% of carbon fiber produced today is derived from solution-spun polyacrylonitrile (PAN) precursor fiber. PAN based carbon fiber offers high toughness at minimal density for lightweight structural applications. On the other hand, mesophase pitch is another precursor fiber, which allows for the production of extremely high modulus and thermal conductivity carbon fiber at minimal density – largely at the expense of toughness in comparison to PAN-derived carbon fiber. Yet pitch-precursor-derived carbon fiber offers some key advantages. First, pitch can be melt spun, whereas PAN is solution spun. Melt spinning is simpler than solution spinning, which requires immense amounts of water and solvent, as well as energy for solvent recovery and water treatment. Second, pitch offers a superior carbon yield, up to 80 wt.% conversion, while PAN offers approximately 50% conversion. And third, pitch does not require complex tensioning during the thermal conversion as does PAN. Pitch is comprised largely of polyaromatic hydrocarbons. Coal tar recovered from metallurgical coking is already utilized to make pitch – an isotropic coal tar pitch. This material is typically utilized in the production of carbon and graphite electrodes for primary aluminum production and steel recycling. However, highly aromatic, isotropic coal tar pitch is quite an ideal precursor for the production of carbon fiber.

Here we report on our work utilizing coal tar pitch, stemming from recovered overheads from the coking of metallurgical coal, as a precursor for carbon fiber. The starting coal tar pitch contained less than 1 wt.% quinoline insolubles (QI). It was thermally upgraded to a mesophase pitch with a softening point temperature of approximately 300 ºC and a mesophase content of > 80 %. The mesophase was melt spun into precursor fiber, then oxidized, carbonized and graphitized. The final carbon fiber properties and morphology will be discussed. Aspects of the overall value proposition of coal to carbon fiber will also be addressed.

5.2 The Effect of Coal-Derived Graphene Nanomaterials in Cementitious Materials

Yuan Gao, Viet Hung Pham, National Energy Technology Laboratory and Leidos Research Support Team; Richard E. Spaulding, National Energy Technology Laboratory; Jennifer Weidman, Congjun Wang, National Energy Technology Laboratory and Leidos Research Support Team; Barbara Kutchko, Christopher S. Matrana1, National Energy Technology Laboratory; USA.

Graphene nanomaterials are promising additives for cementitious composites, due to the improvements they impart on the mechanical, electrical and thermal properties of the material. Currently, it is cost-prohibitive to use commercially-available graphene in composites, but new manufacturing techniques with coal are reducing graphene costs and making the use of nanomaterial composites in construction applications economically feasible. In this study, graphene nanomaterials have been synthesized from different ranks of coal and incorporated into cementitious materials. The cure properties, mechanical properties, microstructure and durability have been evaluated. Low loadings (~0.01-0.1 wt%) of graphene-additive improve the compressive strength, flexural strength and modulus of elasticity for the cementitious composites. These properties are linked to microstructure changes using XRD, TGA and SEM/EDS. In addition, the porosity and permeability have been investigated to evaluate the durability of the cement composites.

5.3 Coal Plastic Composite Materials for Construction Applications

Yahya Al-Majali1, Jason Trembly, Ohio University; Keerti S. Kappagantula, Pacific Northwest National Laboratory; Clive Chirume, Samuel Forshey, Ohio University; USA.

This study investigated the utilization of coal as a filler in plastic composites for use in construction applications. With filler content ranging from 40-70 wt. %, Coal Plastic Composites (CPC) incorporated with three types of coal including Pittsburgh No. 8, Kittanning coal and Powder River Basin (PRB) coal were evaluated and compared to commercially available Wood Plastic Composite (WPC) decking materials. The mechanical properties of CPC samples synthesized using melt-mixing followed by injection molding were compared to commercially available WPCs. In addition, flammability and service life tests such as Flash Ignition temperature (FIT), Self-ignition temperature (SIT), rate of burning and Oxidation Induction Time (OIT) were conducted as per ASTM D1929, ASTM D635, and ASTM 3895 standards, respectively. Mechanical testing results indicate CPCs possess higher flexural strength and comparable flexural modulus in comparison to commercial WPC decking products. CPCs also show flammability rating advantages as CPCs possess higher FIT and SIT in comparison to WPCs. Depending on the type of coal, the rate of burning of CPC was ranged from 15-20 mm/min, whereas the WPC rate of burning was ranging from 30-40 mm/min. With no antioxidant added to the CPCs, CPC OIT determined by differential scanning calorimetry (DSC) was comparable and in some cases higher than the WPCs. Further, process simulations and life cycle studies indicate CPC products are more economically viable, while emitting lower carbon emissions during manufacturing. The preliminary results of the current study show CPC as an economically viable and better-performing substitute for WPCs. In addition, it is anticipated that the CPC will have better resistance to water absorption, fungal attack and insect attack. The presentation will also present recent results in scaling CPC manufacturing using commercial extrusion equipment.

5.4 Partial Replacement of Cement, Aggregates and Natural Sand by Treated Oil Shale Ash in Concrete Mixtures

Haim Cohen, Ben-Gurion University of the Negev; Yaniv Knop, Ariel University; Julio Subovich, Environmental Services Company Neot Hovav Industrial Council; ISRAEL.

Several recent studies have shown that coal fly ash (produced as a residue in Israeli utilities) is an excellent scrubber and fixation reagent for acidic wastes both for inorganic and organic toxic reagents. In addition, the aggregate product, formed via the scrubbing process could be used as a partial substitute of natural aggregates, sand and original cement in industrial concrete mixtures. The concrete product was qualified as a green product according to the European Compliance Test 14257.

On the other hand, oil shale bottom ash can't be used as aggregate or cement replacement, because of the high amount of CaO. The reaction of the water in the concrete mixture with the calcium oxide in the oil shale to form Ca(OH)2 will cause a dramatic temperature raise, increased water demand in the concrete mixture and significant cracks of the hardened concrete mixture. In the current study, it was shown that acidic chemical treatment of the oil shale ash, enables to obtain treated oil shale ash which can be used as partial replacement of both natural aggregates and sand and also as partial replacement of the original cement. Furthermore, thermal treatment (in the range of 600-1100oC) improved the pozzolanic performances of the oil shale ash, so that the ash can be used to replace a greater amount of original cement and to replace all the amount of other active chemical additives, as slag in the cement or concrete production. The results obtained in the current study, can improve significantly the utilization of oil shales as a fossil fuel in the power industry and the use of the oil shale product, as an effective material as one of the main construction materials.

5.5 Development of X-MAT® Coal Core Composites for Roofing Materials and Lithium Ion Battery Anode Applications

William Easter, Semplastics, USA.

Coal has historically been used for electrical power generation and in the production of steel. However, recent X-MAT® Research and Development activities have resulted in an alternative use for raw coal particles as a key component for roof tiles used in the housing industry. X-MAT technology combines proprietary chemical formulations with raw coal powders (approximately 70% by mass of the composite) and transforms these materials into an inert coal core composite. Even though a key component is flammable coal particles, the coal core composite does not burn in an open flame due to the transformation process. The Department of Energy National Energy Technology Laboratory awarded Semplastics a Phase I Small Business Innovative Research (SBIR) grant in 2018 to continue recent X-MAT R&D activities with coal. The specific purpose of this DOE-funded research is to produce coal-core composite roof tiles, which have key advantages in weight, fire resistance, and durability over the conventional alternatives. In addition, Semplastics set up a battery lab in February 2019 to develop anodic materials for lithium battery applications. Several of the experimental battery anode formulations also use coal particles combined with proprietary chemical formulations. Early experimental results indicate that these coal core composites have higher specific capacities than graphite which is the current anodic material of choice for lithium ion batteries. This talk will highlight the progress and challenges experienced in the roof tile project as well as initial results of the coal core composite anodic experimental results.

SESSION 6
CLEAN COAL AND GAS TO FUELS II
Diane Revay Madden and John Duddy

6.1 Promoter Effect on Methanation Activity of Nickel Catalyst Prepared by Impregnation-Co-Precipitation Method

Enkhsaruul Byambajav, Co-author: Buyan-ulzii Battulga, Oyunbileg Galindev, National University of Mongolia, MONGOLIA.

Nickel catalysts supported on γ-Al2O3 were prepared by the method of impregnation-co-precipitation. Effect of Fe, Co and Fe-Co metal promoters were tested for catalytic methanation performance using a fixed bed reactor under a pressure of 3 atm of H2 and CO with a molar ratio of 3:1. The prepared catalysts (Ni/γ-Al2O3, NiFe/γ-Al2O3, NiCo/γ-Al2O3, NiFeCo/γ-Al2O3) were characterized by N2 adsorption-desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM-EDX) and X-ray photoelectronspectroscopy (XPS). Nominal amount of total metals in every catalyst was estimated by 20 wt%, and content of added promoter metal was 5 wt% in a catalyst. After addition of metal promoter, the activities of the catalysts were improved comparing to the Ni/γ-Al2O3 without any promoter. Initial temperature for CH4 formation was decreased according to the order: Ni/γ-Al2O3> NiFeCo/γ-Al2O3 >NiFe/γ-Al2O3> NiCo/γ-Al2O3, as shown in Figure 1. Whereas the Ni/γ-Al2O3 catalyst gave the maximum CO conversion of 97.8% and CH4 selectivity of 94.1% at 4000C, the NiCo/γ-Al2O3 performed the same activity at 3000C of reaction temperature. The results of catalyst characterization revealed that the metal promoters improved dispersion of nickel catalyst, and increased porosity. SEM and XRD analysis of the cobalt promoted Ni catalyst proved the highest dispersion of nickel and the smallest particle size in the NiCo/γ-Al2O3 resulting in the prominent catalytic performance.

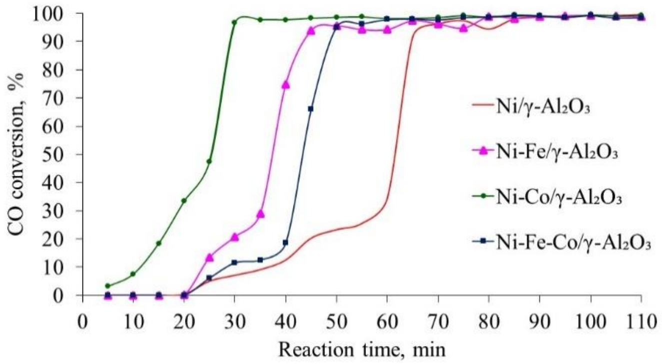

Figure 1. Catalytic performance of Ni/γ-Al2O3 and different metal promoted Ni/γ-Al2O3 catalysts at 350°C

6.2 Effect of Preparation Method of CeO_2 Support on CO Methanation Performance

Anning Zhou, Ning Yan, (Yagang Zhang, Zhiyuan Yang, Xi'an University of Science and Technology, CHINA.

Along with the fast development of the society and economy, natural gas is becoming an important role in clean energy strategy. Synthetic natural gas (SNG) from coal is one of the important ways to solve the shortage of natural gas in China. The development of the coking resistant catalyst for CO methanation is becoming a hot issue. In order to explore CeO2 support structure effect on Ni/CeO2 catalysts, the different morphologies and structure of CeO2 were prepared by using hydrothermal method, microwave method and homogeneous method, and the preparation conditions were optimized. Preparation method and conditions have a significant effect on the morphology and structure of CeO2. Ni/CeO2 catalysts were prepared by ammonia evaporation method. The catalysts and supports were characterized by HRTEM, XRD, H2-TPR and so on. The effect of the morphology and structure of CeO2 on the catalytic activity of Ni/CeO2 catalyst for CO methanation was investigated in a fixed bed reactor.

6.3 Simultaneous Production of Syngas and High-Purity Hydrogen Using Calcium-Iron Based Oxygen Carriers for Chemical Looping Reforming Process

Vedant Shah, Deven Baser, L.-S. Fan, The Ohio State University, USA.

Chemical looping reforming is an attractive process that can be used for conversion of hydrocarbons into syngas, which can ultimately be used for producing liquid fuels through Fisher-Tropsch process. The work done here focuses on simultaneous generation of syngas and high-purity hydrogen using a two-reactor chemical looping system, thus obtaining two value-added products with economic advantage through process intensification.

The use of calcium ferrite (Ca2Fe2O5) as an oxygen carrier particle for chemical looping reforming system has been proposed in this work. The material used has brownmillerite type structure with high ionic conductivity, thus allowing rapid transport of oxygen ions through the material ensuring excellent reaction kinetics.

Thermodynamic software Factsage v7.3 was used to find suitable support material to be used along with the active metal oxide and samples were prepared accordingly for carrying out experiments in thermogravimetric analyzer (TGA) and fixed bed. Methane was used to reduce the samples while producing syngas with high selectivity and almost complete methane conversion. The reduced samples were then oxidized using steam/CO2 to regenerate the material back to original oxidation state. The oxygen carrier material did not show any degradation/phase change even after it was subjected to extended redox cycles, thus suggesting very long lifetime of the material. Temperature programmed reduction (TPR) experiments were also carried out using TGA to assess the performance of different oxygen carrier compositions against each other. Thermodynamic analysis of various reactions involved in the proposed chemical looping system was done to understand the interaction between various gaseous and solid species amongst each other. Solid samples obtained after different experiments were subjected to characterization, which enabled to understand the conversion of starting phase into other different phases. SEM/EDS was used to observe any morphological changes and XRD was used for phase identification and quantification.

Thermodynamic analysis and experimental results prove that calcium ferrite is an attractive oxygen carrier for methane reforming to produce syngas and hydrogen. Occurrence of structural changes and tolerance to carbon deposition from methane decomposition are major challenges that must be overcome to ensure this material is economically viable without the need for frequent replacement.

6.4 Theoretical Study on Mechanism of Hydrodeoxygenation of Dibenzofuran Catalyzed by Pt Based Catalyst

Zi-Zheng Xie, Xing-Bao Wang, Jie Feng, Wen-Ying Li, Taiyuan University of Technology, CHINA.

The low temperature coal tar and coal liquefaction oil can be used as fuel. But the high oxygen content in these oils results in poor thermal stability and low heating value. Catalytic hydrodeoxygenation is an efficient way to remove the oxygen atom and upgrade the quality of these oils. However, limited knowledge about the mechanism of HDO stymies the rational design of more efficient and stable catalysts. Dibenzofuran (DBF) is an oxygenated model compound of the low temperature coal tar and coal liquefaction oil. The hydrodeoxygenation of DBF catalyzed by Pt based catalyst has been widely studied. However, the corresponding reaction mechanism is still under debate. The current debate focusses on two issues: how opening five-membered ring and how deoxygenating of DBF. Density functional theory calculations were performed to understand the reaction mechanism of hydrodeoxygenation of DBF on the Pt(111) surface. Calculated energetics and activation barriers (Figure 1) indicate that the ring-opening reaction of five-membered ring in tetrahydrodibenzofuran is easier (TS1, 0.40 eV) than hexahydrodibenzofuran (TS2, 1.25 eV). This could be ascribed to the stronger interaction with the Pt(111) surface and little deformation energy of tetrahydrodibenzofuran, which contains an unhydrogenated double bond. Then the intermediates are hydrogenated to 2-cyclohexylphenol (CHPOH). The nonconsecutive hydrogenation of CHPOH could result in a multiple radical species, which can be steadily adsorbed on the Pt (111) surface and have little deformation energy during the hydrogenation reaction. Thus, CHPOH is prone to go through the nonconsecutive hydrogenation rather than consecutive hydrogenation. The dehydroxylation reaction of the intermediate formed by adding five H atoms to the phenyl ring of CHPOH has a lower energy barrier (TS3, 1.53V). However, the dehydroxylation reaction of cyclohexylcyclohexanol has a higher energy barrier (TS4, 2.04 eV). For the hydrodeoxygenation of DBF on Pt (111) surface, the dehydroxylation reaction is the rate-determining step. We hope these investigations can provide a theoretical basis for designing new catalysts for HDO of coal based oils.

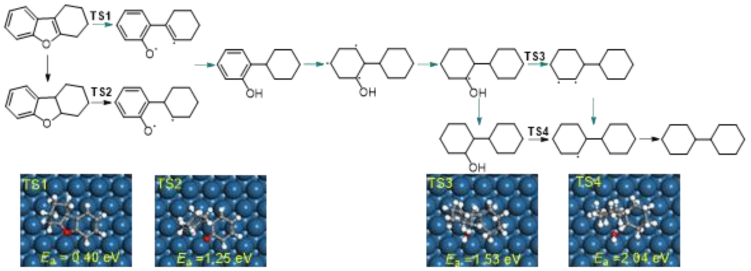

Figure 1: The possible pathways of the hydrodeoxgenation of tetrahydrodibenzofuran and hexahydrodibenzofuran. Some transition state structures and corresponding energy barriers also are shown.

6.5 Selective Hydrogenation of CO_2 Over ZSM-5-Based Tandem Catalysts

Marc D. Porosoff, University of Rochester, USA.

CO2 hydrogenation is a reaction under investigation for production of synthetic chemicals and fuels as an alternative to petroleum-based processes. However, the selectivity towards hydrocarbons, and specifically desirable olefins, is generally characterized by the highly-unselective Anderson-Shulz-Flory (ASF) distribution. To avoid the energy-intensive, post-reaction separation steps, researchers have recently attempted to selectively produce light olefins (ethylene and propylene) during CO2 hydrogenation via dual-functional, tandem catalysts, which take advantage of secondary reactions within zeolites (C-C bond formation and C-H bond scission), thus yielding higher selectivity to light olefins.[1]The active phase of tandem catalysts generally consists of a mixed metal oxide, which is either dispersed on or physically mixed with an aluminosilicate zeolite. The function of the metal oxide is to activate the CO2 to a methanol or hydrocarbon intermediate. The zeolite can restrict hydrocarbon products to a narrow size distribution by sterically limiting diffusion within the micropores and cracking larger paraffins into olefins over Brønsted acid sites (i,e. H-ZSM-5) [4]. Tandem catalysts have recently become the subject of intense investigations, but guidelines are unavailable for selection of the active phase, zeolite and promoters to achieve high selectivity towards light olefins. As such, it is necessary to develop a fundamental understanding of the structure-property relationships for CO2 hydrogenation. Our initial work is focused on studying the Si/Al ratio and method of introduction of extra-framework cations in the ZSM-5 topology to control hydrogenation of the mildly acidic CO2 molecule. The zeolites are impregnated with cobalt (Co), and the potassium (K) promoter is introduced either via co-impregnation or ion exchange (IE), to demonstrate if the Si/Al ratio and method of introducing K has a predictable effect on CO2hydrogenation to olefins. In our work, for catalysts prepared via co-impregnation, the selectivity towards CO decreases while that of CH4, C2-C4 olefins, paraffins and C5+ hydrocarbons increase with increasing Si/Al ratio. Conversely, for catalysts with K first introduced via IE, the selectivity to all products remains relatively constant as the Si/Al ratio increases. These distinct observations of selectivity, combined with acid site titration, insitu XAFS and FTIR, suggest that ion exchange can eliminate the Brønsted acid sites in ZSM-5, thereby mitigating the effect of Si/Al ratio.

SESSION 7
GASIFICATION TECHNOLOGIES II
Rolf Maurer and Harvey Goldstein

7.1 Reactive Separation of H_2S from Syngas with Coproduction of Hydrogen and Elemental Sulfur Using Thermo-Catalytic Sulfur Capture Process

Kalyani Jangam, Sourabh Nadgouda, Lang Qin, Yu-Yen Chen, L.-S. Fan, The Ohio State University, USA.

Most of the syngas utilization processes demand sulfur concentration <10 ppmv due to low sulfur tolerance of catalysts involved. Sulfur removal is conducted by converting sulfur compounds in coal into H2S, followed by absorption of H2S in solvents like methyl diethanolamine (MDEA) and/or Selexol in acid gas removal (AGR) process. The high concentration H2S stream obtained in AGR process is then oxidatively decomposed in Claus process for elemental sulfur recovery. However, the process efficiency of AGR and Claus process is reduced due to high parasitic energy requirement. More importantly, H2 content of H2S is lost as water vapor during Claus process due to its oxidative-decomposition route. In this work, a thermo-catalytic sulfur capture (TCSC) process is developed based on the chemical looping approach for advanced H2S processing, allowing non-oxidative decomposition of hydrogen sulfide into hydrogen and elemental sulfur. The TCSC process consists of two primary steps: sulfidation and regeneration. In the sulfidation step, iron sulfide (FeS) catalytically decomposes H2S into hydrogen and sulfur with latter getting captured within FeS, producing sulfur rich phase–FeSx (where, x>1). The captured sulfur is then removed in the regeneration step by thermally decomposing FeSx into FeS in inert atmosphere and at a higher temperature and/or lower pressure than the previous reactor. Thus, TCSC process drastically cuts down the required number of processing units over conventional H2S separation and treatment process scheme. However, experimental study shows that the reaction conversion of H2S is limited by the slow reaction kinetics. First-principles density functional theory (DFT) simulations show that addition of dopants can modify the surface electronic structure of FeS, causing a decrease in the activation energy of the rate-limiting step. Fixed bed experiments were performed to corroborate the DFT simulation results and improvement in performance of FeS was demonstrated. Thus, this work offers a cost-effective technology with a potential to replace the conventional H2S separation and treatment scheme.

7.2 Full-Scale Dry Solids Pump Testing Up to 500 Psi and Techno-Economic Evaluation When Installed in a Quench Gasifier

Timothy Saunders, Joseph Caravella, Gas Technology Institute; Greg Weber, University of North Dakota, USA; Christopher Higman, Higman Consulting, UK.

The gasification industry has been seeking a solution for feeding carbonaceous materials into high gas pressure environments since the oil shale program of the seventies. Existing feeding technology handicaps the implementation of advanced combustion systems through limiting operating pressure levels below optimum, unreliable and inaccurate feed control, and the need for very large footprints and structure heights to incorporate the stacked lock hoppers that currently are the only feed solution. These attributes contribute to high capital cost, high operating cost and a proven low level of feed reliability. Additionally, existing feed systems are very inflexible in their ability to handle a wide range of coal types, particularly low rank coals such as sub-bituminous and lignite. For advanced combustion systems to achieve their potential, highly controlled and accurate feeding along with feedstock flexibility is critical to reduce operating costs and make the combustion systems competitive with traditional power plants.

This high-pressure feed solution has been promoted and supported by the US Department of Energy National Energy Technology Laboratory (NETL). The project was initiated by Pratt and Whitney Rocketdyne (PWR), and later acquired by the Gas Technology Institute (GTI), who is finishing the development program. PWR initially designed and manufactured a full-scale Dry Solids Pump (DSP). This direct-to-commercial scale approach was intended to reduce the development time for the DSP system. The full-scale DSP was manufactured and installed in a test stand at the Energy & Environmental Research Center (EERC) in Grand Forks, North Dakota. A test program was undertaken to verify the pump's ability to inject pulverized coal into high gas pressure however needed iterative development changes created a challenge due to the time to dismantle, cost to modify, and time and cost to reassemble the full-commercial-scale pump. To address this challenge, a subscale version of the DSP was built to allow rapid and lower cost optimization of the internal mechanisms of the machine and enhancements to the configuration to improve performance and efficiency. As part of this program a range of coals from anthracite through bituminous to sub-bituminous, lignite and biomass blends with the previous coal feeds was tested in the subscale pump. The subscale DSP successfully injected these coals and coal-biomass blends into a high-pressure environment (150 psi for the subscale DSP). The DSP design and configuration modifications, developed through the subscale program to handle these wide-ranging fuel types, were then incorporated into the original full-scale DSP. The modified full-scale DSP was recommissioned in 2018 and tested at a range of pressures up to 500 psi, the hardware's design pressure limit.

This paper will present details on the subscale pump test program and the resulting modifications made to the full-scale DSP. Results from the full-scale pump tests will be presented along with the anticipated commercial DSP configuration which was developed based on the test results. A Techno Economic Analysis (TEA) was undertaken as part of the program. The TEA identified cost benefits arising from use of a DSP in commercial gasifier applications using both dry syngas and quench cooling. The results of the TEA will be presented.

7.3 Preparation and Characterization of NiFeAl Oxygen Carrier for Coal Chemical Looping Combustion

Ze-Hua Wei, Jie-Ying Jing, Dao-Cheng Liu, Jie Feng, Wen-Ying Li, Taiyuan University of Technology, CHINA.

CO2 emission reduction is of great practical significance for slowing down the greenhouse effect and improving the natural environment Chemical looping Combustion (CLC) is a new coal-based carbon capture technology. Compared with the existing CO2 capture technology, CLC technology has the characteristics of high system efficiency and low cost of CO2 capture. In this process, oxygen carrier can not only provide oxygen source, but also serve as a heat carrier to circulate between air reactor and fuel reactor. Moreover, oxygen carrier can also act as a catalyst for tar cracking, coal char gasification and other reactions after modification. Therefore, the research on high performance oxygen carrier has always been the focus and difficulty of coal chemical looping combustion technology. Currently, Fe2O3, NiO, CuO and MnO2 are widely employed as the oxygen carriers. Due to its advantages of low price, abundant resources, and environmental friendliness, Fe-based oxygen carriers have attracted extensive attention and are considered to be very promising oxygen carriers for industrial applications. However, when the single iron oxide is used as an oxygen carrier, it is easy to agglomerate at high temperatures, leading to the decreasing activity of oxygen carrier with the increase of cycle times. In order to improve its cyclic stability, Al2O3 is widely introduced to improve its anti-sintering performance. Besides, a multicomponent oxygen carrier, such as Ni-Fe bimetallic oxide, is often prepared so as to enhance its activity by the synergistic effect of various metal oxides. In this work, we try to combine Al2O3, and Ni-Fe bimetallic oxide together so as to obtain an oxygen carrier with high activity and cyclic stability. If the three components are simply mixed together, there might be some problems, such as reaction of the active component with the inert component, and phase separation etc. In order to solve the above problems, we would use the spinel structure to incorporate these three components into a crystalline structure, which could not only take the full advantages of each component but also maintain the stability of its structure. First, the NiFeAl oxygen carriers with spinel structure were synthesized by sol-gel method and coprecipitation method, then we studied the structure and reduction property of the NiFeAl oxygen carriers by various experimental methods, including X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA), H2-temperature programmed reduction (H2-TPR) and so on. Results show that the NiFeAl oxygen carriers synthesized by sol-gel method possessed the best reactivity. It is found that the dosage of NiFeAlO4 oxygen carrier in CLC reaction plays an important role. The existence of NiFeAlO4 oxygen carrier promoted the combustion reaction of coal. As the mass ratio between oxygen carrier and coal gradually increases, the carbon conversion rate of coal gradually increases, so does the total gas product. Moreover, with the increasing mass ratio between oxygen carrier and coal, the relative concentration of CO2 in the gas product first decreases and then increases, which is due to the providing oxygen capacity of NiFeAlO4 oxygen carrier.

7.4 Process Analysis of Chemical Looping Coal Gasification for Dimethyl Ether Synthesis

Fanhe Kong, Mandar Kathe, Andrew Tong, Pengfei He, Liang-Shih Fan, The Ohio State University, USA.

Coal is both an essential industrial energy source and a starting material for chemical synthesis. The conversion from coal to liquid fuels and value-added chemicals is one of the research areas that has attracted intensive research efforts. In this paper, an intensified process approach of converting coal into dimethyl ether (DME) using chemical looping strategy is investigated. This novel process consists of a chemical looping gasification section designed at The Ohio State University (OSU), followed by methanol and DME syntheses. A process analysis and optimization using ASPEN Plus and ASPEN Energy Analyzer is conducted, with the objective to maximize the coal to DME conversion efficiency through the intensified chemical looping design. In the chemical looping gasification process, two reactors, namely a reducer and a combustor are used to convert coal into syngas. In the reducer, coal reacts with an iron-based metal oxide oxygen carrier (OC) to form a mixture of H2 and CO while the OC is reduced into a lower oxidation state. The reduced OC is then transported into the combustor to be regenerated to its original oxidation state using air as the oxidant before starting the next cycle. Compared to conventional gasification, this process can eliminate the energy and cost intensive air separation unit and replace the expensive gasifier with the chemical looping reactor system which has a milder operating condition and is easier to operate and control. The syngas produced from the chemical looping system will then be used for methanol and DME syntheses using conventional unit operations. The heat and material balances of the coal to DME process are calculated using ASPEN Plus. The process heat integration and heat exchanger network design are conducted in ASPEN Energy Analyzer. Process simulation shows that the chemical looping gasification can achieve a 5-10% higher syngas yield than conventional gasification, which corresponds to the same increase in DME productivity using equal amount of coal as feedstock. The process heat integration shows that the whole process can operate under autothermal conditions, i.e. no external heat source is needed to maintain the operation. The high DME yield and efficient heat integration translate into a high effective thermal efficiency (ETE) of the chemical looping coal to DME process, which is ~10% higher than the coal to DME process based on conventional gasification. The coal gasification process has been demonstrated in a 25 kWth sub-pilot unit with multiple operating conditions and acquired steady state performance data, which show close matches with simulation results, validating and corroborating this novel chemical looping system design from a practical perspective.

7.5 Chemical Looping Gasification of Lignin with Bimetallic Oxygen Carriers

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Chemical Looping Gasification (CLG) is a promising technology to produce syngas from renewable biomass material without the need for upstream air separation and downstream CO2 capture/sequestration. Lignin is the main component of biomass and the second most abundant organic materials on the planet. In addition, it is a waste by-product from integrated bio-refinery. Traditional gasification of biomass have the disadvantages of low gas yield and the highest tar yield. Four bimetallic oxygen carriers (CaFe2O4, CaMn2O4, BaFe2O4, BaMn2O4) are systemically studied on CLG of biomass-based lignin as fuel source. Thermodynamic analysis and online mass spectral data indicated that BaFe2O4 demonstrated the best ability to selectively gasify lignin and have good regeneration, which made it very attractive for chemical looping partial oxidation of biomass in realistic applications. All oxygen carriers studied showed the ability to be fully regenerated in air after reduction. Furthermore, CO2 addition not only increased production of CO due to reverse Boudouard reaction (C+CO2→CO), but also accelerated the kinetics of gasification process. The overall process achieved negative CO_2 emission, which greatly intensified the CO2 capture efficiency of biomass-CLG.

SESSION 8
POWER PLANTS II
Massood Ramezan and Ting Wang

8.1 Development of a Mild Gasification Model for Use in an Integrated Mild/Partial Gasification Combined (IMPGC) Cycle

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In simulating the gasification process using numerical models, the most difficult part to fully understand is volatile cracking. This is for several reasons: 1.) The exact chemical conformations and configurations of the volatile matters within the fuels are unknown, and there is little to no data available within the literature about what the chemical structures of the volatiles are for many types of coals before cracking occurs. 2.) The enthalpies of formation of the volatiles are also unknown for similar reasons. Finally, 3.) due to the above, there is(are) no universally-agreed-upon chemical reaction equation(s) that govern volatile cracking. (In real practice, the exact chemical equations would vary greatly with feedstock composition). In developing a functional thermodynamic model for an Integrated Mild/Partial Gasification Combined (IMPGC) cycle system, the volatile cracking process is more complex because, unlike the full gasification process, the end products are not known. It is necessary to develop a numerical model that can predict the resulting syngas composition and equilibrium temperature of the resulting mild syngas produced by the mild/partial gasification process. As such, a complete understanding of volatile cracking is vital. This paper focuses on discussing the procedure for calculating the above-mentioned two items for a mild/partial gasification process and how reasonable the results of this endeavor hold up compared to what is expected in reality. The composition can be obtained using a unique application of mass, energy, and species balances, and the temperature can then be obtained in a manner similar to finding a combustible substance's adiabatic flame temperature. The results show that the model can successfully yield results that are in-line with our intuition of what is to be expected from mild gasification, and, though somewhat crude, the model itself is flexible enough that additional assumptions or modifications can be added as new experimental/theoretical data becomes available. The equilibrium temperature calculated ranges from 790-1170°F, and the heating value of the syngas is anywhere from 1.5-2.5 times that of traditional, fully-gasified syngas.

8.2 Generation Efficiency Enhancements by Non-Ablative Fouling Control Coatings

Vinod Veedu, Matthew Nakatsuka, Erika Brown, Oceanit, USA.

In the constant push for more efficient plant operation, the persistence and stubborn resilience of biological fouling has proven to be a long-lasting challenge. While most fouling is relatively easy to remove via a variety of unsophisticated techniques, no single, economically advantageous technology has been widely adopted. While the overall effect of a biofilm on flow properties or on heat transfer is relatively small early on in accumulation phases, such growths can act as catalyst sites for additional macro biogrowth and marine attachment, significantly accelerating losses in performance, increasing wear-and-tear on key power plant components, and requiring additional off-line/down-time for manual cleaning.

This paper details the use of an in-situ applicable nanosurface treatment on a number of different power plant substrates to control fouling. Because of the extremely low effective surface roughness and surface energy, the treatment enables adhered biologicals and bacteria to be more easily dislodged by water or flow, while simultaneously reducing frictional drag, enabling faster stream flow, and further promoting effective self-cleaning.

The surface treatment was shown to be extremely easy to utilize on concrete-lined steel, on shell-and-tube heat exchangers, and on plate-and-frame exchanger geometries. The nanotreatment has a number of advantages in application; its low volatility and non-toxic nature allows it to be used in physically confined areas; tunable viscosity allows for it to be applied via spray or brush, and it can be modified for strong adhesion to stainless steel, titanium, cement mortar and epoxy.

As part of this paper's case study, the effects on plant operation after adopting the surface treatment will be detailed; benefits found over the study period include: significant reductions in manpower dedicated to cleaning, longer operational cycles between maintenance, shortened downtime during maintenance operations, ability for the treatment to be spot repaired in-place, and improved intake flow with reduced pump load.

8.3 Coal-Fired Direct Injection Carbon Engine (DICE) and Gas Turbine Compound-Reheat Combined Cycle (GT CRCC)

S. C. Gülen, Bechtel Infrastructure & Power, Inc., USA.

This paper describes a modular, high-efficiency coal-fired power plant comprising reciprocating internal combustion engines combined with gas/steam turbines in a combined cycle configuration. The proposed plant concept, the coal-fired DICE – Gas Turbine (DICE-GT) Compound-Reheat Combined Cycle (CRCC), is a combined cycle power plant comprising

- A multiplicity of coal-fired reciprocating internal combustion engines (RICE), which is commonly referred to by the acronym DICE (Direct Injection Carbon Engine);
- A natural gas-fired gas turbine (turbine and combustor);
- A heat recovery steam generator (HRSG);
- A steam turbine generator (STG);
- An integrally-geared and intercooled process compressor.

Utilizing coal-water slurry as fuel, reheat combustion with high-efficiency engines in a combined cycle configuration is thermodynamically the most efficient fossil fuel-fired heat engine configuration. In its ultimate embodiment with most advanced engine and gas turbine components, more than 50% net LHV is possible at a rated output of around 120 MWe. An introductory version utilizing hot off-the-shelf gas expanders can provide the same rated output at 45+% net LHV. The paper describes several variants of the technology with and without post-combustion capture.

8.4 Dynamic Modeling and Control Strategies for Flexible Operation of a 10 MWe Supercritical CO_2 Recompression Closed Brayton Cycle

Stephen E. Zitney, Jacob T. Albright, Gaurav Mirlekar, Eric A. Liese, National Energy Technology Laboratory, USA.

Supercritical carbon dioxide (sCO2) Brayton power cycles are an attractive alternative to conventional steam-based Rankine power plants. The properties of the sCO2 working fluid allow for substantially more compact turbomachinery and a power cycle with the potential for higher thermal efficiencies and greater operational flexibility. Due to these advantages over traditional systems, the U.S. Department of Energy, under its Supercritical Transformational Electric Power (STEP) Program, is working with industry and research partners to design, build, and operate an sCO2 pilot plant test facility that has a 10 megawatt electric (MWe) net power output. The sCO2 pilot plant will be designed as a recompression closed Brayton cycle (RCBC) that uses a natural gas-fired furnace as the indirect heat source. The new facility will support the demonstration of systems integration, performance, operability, and controls for the future commercialization of utility-scale sCO2 Brayton power cycles.

In this presentation, a pressure-driven dynamic model of a 10MWe indirect sCO2 RCBC is described, along with its use for developing effective control strategies for efficient, flexible operation. Considering Carnot's rule, the RCBC efficiency is maximized by keeping the ratio between the hot turbine inlet temperature (TIT) and the cold main compressor inlet temperature (MCIT) as high as possible. To maintain cycle efficiency near its maximum during RCBC turndown and ramp-up operations, this study uses sliding-pressure operation via inventory control wherein sCO2 is removed and added, respectively, from the closed cycle. A control strategy is developed that regulates the natural gas fuel inlet and the sCO2 inventory tank inlet and outlet valves in a fast and effective manner to achieve the TIT control objectives while following a new cycle power setpoint. Similarly, cooling water flow control is used to maintain the MCIT at its minimum design point slightly above the critical temperature of CO2. In addition, the flow split between the main compressor and bypass compressor streams is controlled to increase cycle efficiency during flexible operations. The presentation will highlight dynamic simulation results analyzing RCBC performance and control for maximizing efficiency during flexible operations.

SESSION 9
COAL SCIENCE II
Atsushi Ishihara and Leslie Ruppert

9.1 The Yampa Coalfield, Northwestern Colorado, USA- A Western U.S. Analogue of the Appalachian Fire Clay Coal?

Allan Kolker, Brian N. Shaffer, Leslie F. Ruppert, Clint Scott, U.S. Geological Survey; Charles N. Thompson, Thompson Geo Service, Inc.; USA.

Among U.S. coals and coals of the Appalachian Basin, the Fire Clay coal of eastern Kentucky is noted for its enrichment in rare earth elements (REE), making it one of the most promising exploration targets for recovery of critical REE from secondary sources. REE enrichment of the Fire Clay coal is considered to result from inclusion of a prominent, laterally persistent tonstein (coal-hosted volcanic ash bed), together with groundwater leaching of the tonstein to enrich REE contents of coals directly beneath it (Hower et al., 1999, Int. J. Coal Geol. v. 39, p. 141-153). Whereas western coals generally have lower total REE contents than Appalachian Basin coals, recent studies indicate a greater proportion of REE present in lower rank western coals may be readily extractable. This has led to current interest in western coals as potential REE feedstocks.

The Yampa Coalfield of northwestern Colorado contains the Yampa Bed, a laterally extensive tonstein that forms a prominent regional stratigraphic marker (Brownfield and Johnson, 2008, USGS Sci. Inv. Report 2008-5033). The Yampa Coalfield includes three coal-bearing sequences within the Upper Cretaceous Mesaverde Group, with the Yampa Bed occurring within the lower portion of the middle coal group. A preliminary survey of the USGS COALQUAL database shows that 8 of 163 records for the Yampa Coalfield exceed averages for La and Ce in U.S. coal, and five of these records also exceed the average for Y. COALQUAL is dominated by REE-enriched eastern bituminous coals, such that it is uncommon for western coals to exceed REE averages in the database. Compared to other REE, La, Ce, and Y are among the most useful for screening REE contents in COALQUAL because these three REE are among the least impacted by qualified (less than) values included in the database (Lin et al., 2018, Int. J. Coal Geol. v. 192, p. 1-13).

To investigate the influence of volcanic activity that produced the Yampa Bed on REE contents of associated coals, new reconnaissance sampling was conducted for coals in the stratigraphic interval just above the Yampa Bed. Two coal benches were sampled within an active underground mine in the Yampa Coalfield, Routt County, Colo. The uppermost bench contains a 0.3 m thick facies that resembles a re-worked tonstein apart from the Yampa Bed. The lower bench was subsampled in three facies: 1) a mineral-rich band directly underlying the upper bench "tonstein" 2) banded vitrinite-rich facies, and 3) an organic-rich siltstone that comprises the floor. In addition to whole coals, samples were designated for float/sink gravity separation at a density of 1.5 gcm-1 to investigate partitioning of REE between raw coal, prepared coal produced for shipment, and waste products of coal preparation.

9.2 Value Addition of Low Rank and Heat Affected Indian Coals for Preparation of Metallurgical Grade Coal by Blending: a Case Study

Prabal Boral, Bodhisatwa Hazra, Ashok K Singh, CSIR-CIMFR, Pradeep K Singh, CSIR-CIMFR, INDIA.

The availability of metallurgical grade coal in India is very scarce. India depends heavily on import for production of steel and the demand of through blast furnace route. The optimal use of metallurgical coals present in India is the need of the hour. To optimize and for sustainable use of indigenous coking coal it is very important to use the available coal/heat affected coals (jhama) in right proportion with prime coking coal. In order to use low rank coal and jhama, an attempt has been made to blend those with prime coking coals for preparation of metallurgical grade coal. To select a proper blend from coals of different ranks and maceral compositions on the basis of chemical parameters alone is sometime very difficult. To optimize the blend proportions for coke making Coal Petrography is used as an important tool. The reflectance of vitrinite is considered as one of the best rank parameters to adjudge the coking propensity with the maceral composition to be used in the metallurgical industry.

In the present investigation, six coals were selected from different seams of Jharia and Raniganj coalfields of Damodar valley basin of India. Out of these six coals, one was low rank coal with mean random reflectance of 0.59 % and one heat affected coal was used for preparation of blend. The volatile matter (VM) content of jhama sample was low (12.6 %) which was compensated by the low rank high VM (32.2 %) coal. Based on chemical parameters and petrographic properties (reflectance and maceral composition), single coals were mixed to make a suitable blend. These single coals and their blends were studied for their rheological properties of carbonization such as Crucible Swelling Number (CSN) and Low Temperature Gray King Assay (LTGK) for their coking propensity. The CSN and LTGK coke type of single coals varied widely from 1 to 4.5 and C to G7 respectively, except the jhama which remained pulvurent in both the tests. Whereas, CSN and LTGK of prepared blend was determined as 3.5 and G1 respectively.

Efforts were made to accommodate maximum amount of low rank coal and jhama for making a blend of metallurgical grade. The highest amount of these low rank coal and jhama could be accommodated in the blend was found to be 15 %. Value addition of inferior coals and jhama was achieved by using only 75 % metallurgical grade coals for preparation of the blend.

9.3 Three Dimensional Aggregated Structural Model of Coking Coal

Yuki Hata, Yoichi Matsuzaki, Takafumi Takahashi and Koji Kanehashi, Advanced Technology Research Laboratories Nippon Steel & Sumitomo Metal Corporation, JAPAN.

Recently, various kinds of coal including subbituminous coal have been used as raw materials of coke for iron making. However, the amount of the subbituminous coal is limited because it has inferior coking property as represented by low dilatation. The coal dilatation is considered as gasification caused by pyrolysis and structural relaxation of aggregated molecules in coal. The aggregated structure of coal is thought to be formed by hydrogen bonds [1], π-π stacking [2], and charge-transfer interactions [3]. However, the relaxation mechanism of aggregated structures has not been clarified in detail. Although there must be some differences between aggregated structure of bituminous coal and subbituminous coal, we have not specified the concrete difference in chemical structure of coal. The aim of this study is to construct three-dimensional aggregated structural model of coking coal to clarify the mechanism of relaxation of coal aggregation by heating. Our approach includes a combination of experimental and simulation. We determined two dimensional average molecular structures for fractions obtained by acetone, pyridine, and magic solvent extraction [4] of a coking coal by using a computer program [5]. On the basis of two-dimensional structures, the three-dimensional aggregated structure of each fraction was constructed by Molecular Dynamics (MD) simulation where the interactions among molecules are considered.

Differential Scattering Calorimetry (DSC) curves of coking coal were presented in Figure 1. We focused on the lowest temperature of the endothermic peaks, because it may be caused by rapid expansions in sample volume. These endothermic peaks were 365 □C for No.1, 382 oC for No.2, and 390 ºC for No.3. Since the endothermic peak is shifted to higher temperature at any heating rate, glass transition temperature of coal also increases with heating rate. We defined the glass transition temperature (Tg) as intersection point between baseline and tangent line of inflection point. Tg were determined to be 337 ºC for No.2 and 352 ºC for No.3, whereas that for No.1 could not be determined because its baseline was ambiguous. Nevertheless, we estimated glass transition temperature at with the minimum heating rate as 315 ºC based on an assumption that glass transition temperature with minimum heating rate can be determined by making approximate linear line.

Two types of three-dimensional aggregated structure models for coal were constructed by MD calculations (Figure 2(a) and (b)). The changes in average specific volume (inverse density) for (a) orthorhombic and (b) cubic cells as obtained by the MD calculations were calculated. We estimated Tg as the point where the thermal expansion coefficient changed. The Tg of three-dimensional aggregated structure models of Figure 2 (a)orthorhombic and (b) cubic cells are 267 ºC, and 298 ºC, respectively. Although both of the calculated Tg values are lower than those estimated by DSC measurements, the calculated Tg for the cubic-cell model is closer to the experimental Tg than that for the orthorhombic-cell model. This result suggests that the cubic model is preferred to the orthorhombic one for the estimation of three-dimensional aggregated structure of coal.

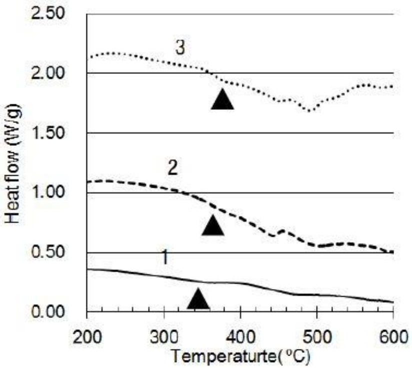

Figure 1 DSC thermograms illustrating the shift of transition temperatures with heating rate of coking coal. Heating rate was 10 ºC/min for No.1, 30 ºC/min for No.2 and 50 ºC/min for No.3, respectively.

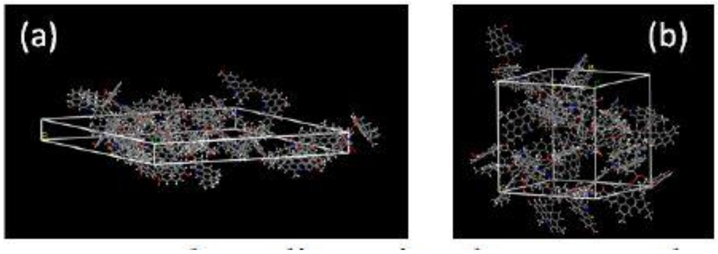

Figure 2 Three-dimensional aggregated structure models of coking coal at 100 ºC as obtained by MD simulations with (a) orthorhombic and (b) cubic

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9.4 Photocatalytic Degradation of Aqueous Colored Chemicals Using Titania and Zirconia-Tellurite Glasses

Atsushi Ishihara, Riko Itou, Ayano Fujita, Tadanori Hashimoto, Hiroyuki Nasu, Mie University, JAPAN.

As transparent glasses pass light well, glasses may have great potential for high photocatalytic activity. However, glasses are not suitable for adsorption of chemicals because they do not have large amounts of pores and therefore photocatalytic activity of glasses has hardly been reported. On the other hand, although it is well-known that TiO_2 is a catalyst with high photocatalytic activity, there are very few reports using ZrO_2 as a photo-catalyst. In this study, we were interested in the possibility of TiO_2-TeO_2 and ZrO_2-TeO_2 glasses as photocatalytic materials. They were prepared by the melt quenching method, and degradation of colored aqueous solutions, which may be exhausted by coal processing, was conducted to observe the photocatalytic activity.

Titania, zirconia and tellurium dioxide were used as starting materials for Ti-Te and Zr-Te glasses. TiO_2 or ZrO_2 and TeO_2 were mixed, melted at 1000°C, pressed at room temperature, and then annealed at 200°C. In order to obtain a more active photocatalyst, Pt of 0.1wt% was added by impregnation method. DTA and XRD measurements were carried out as characterization of the prepared catalysts. As a photocatalytic reaction, the degradation of methylene blue (MB) as a model compound was carried out under irradiation of ultraviolet light for 2 hours. Prior to irradiation, in order to confirm the adsorption / desorption equilibrium of the suspension, it was continuously stirred under a dark air atmosphere for 30 minutes.

$20TiO_2$-$80TeO_2$ and $25TiO_2$-$75TeO_2$ glass samples did not show crystal signals, indicating that they were vitrified. A crystal phase of α-TeO_2 was observed in $20TiO_2$-$80TeO_2$ and $25TiO_2$-$75TeO_2$ glass samples calcined at 600ºC. Two crystal phases, α-TeO_2 and $TiTe_3O_8$ were found when 0.1wt% of Pt was added to $25TiO_2$-$75TeO_2$ calcined at 600ºC (0.1Pt/25Ti-75Te(600)). In blank test, the degradation of MB was 3.2%. 0.1Pt/25Ti-75Te(600) showed the highest degradation rate of MB, indicating that the photocatalytic activity would increase by crystallization of glass with calcination and supporting Pt. The activity decreased in the absence of Pt and calcination.

$ZrTe_3O_8$ signals detected by XRD tended to increase as the Zr content increased. When $ZrTe_3O_8$ was involved in XRD, the degradation of MB proceeded regardless of calcination of glasses. The calcination of glasses increased the crystallization of $ZrTe_3O_8$ and tended to increase the activity.

SESSION 10
VALUE-ADDED PRODUCTS FROM COAL II
Zhiyuan Yang and Evan Granite

10.1 Opportunities and Challenges for A Domestic High-Value Coal Products Industry

Sujit Das, Oak Ridge National Laboratory, USA.

U.S. demand of coal for power generation has declined because of a shift to natural gas, due to lower natural gas prices, and to renewable energy sources. This decline is causing significant economic impacts to the US coal industry. The complex, dense carbon chemical structure of coal, abundant domestic supply, and stable, low price gives it great potential for use in a wide range of value-added non-fuel coal products (e.g., nanomaterials at 20,000–100,000 $/kg and commercial-grade carbon fiber at 22–33 $/kg), as well as in upgraded coal fuels. Of the three major potential coal conversion routes —carbonization, gasification, and liquefaction-exist for the production of high-value coal products, a range of near-term high-value coal products such as pitch carbon fiber, carbon foam, structural/construction materials, and carbon nanomaterials etc. based on the carbonization coal conversion route. Opportunities and challenges in terms of both technical and economic for a viable domestic high-value coal products industry will be reviewed for major products based on the carbonization coal conversion rate. A preliminary technoeconomic analysis of pitch carbon fiber will also be presented which shows the pitch carbon fiber could potentially be a low-cost carbon fiber source to meet the growing demand for carbon fiber reinforced polymer composite applications.

10.2 Preparation of Graphene Oxide-Enhanced Porous Carbon and Its Gas Adsorption Properties

Zhiyuan Yang, Zhuoyue Meng, Hongbin Liao, Jingjing Zhao, Hailong Ning, Xi'an University of Science and Technology, CHINA.

The graphene oxide-enhanced porous carbon was synthesized by a one-step method of activation with low cost. The morphology and porous properties of the composite porous carbon was evaluated by N2 adsorption-desorption and scanning electron microscopy (SEM), while chemical property was determined by Raman spectroscopy. The prepared composite porous carbon exhibits a high Brunauer-Emmett-Teller (BET) specific surface area (SSA) (3140.61 m2 g-1) with the average pore size at 2.51 nm. The composite porous carbon shows excellent adsorption capabilities for CH4 (6.87 mmol g-1) and N2 (3.98 mmol g-1) in the environmental temperature of 303 K and 3 MPa ambient pressure. Furthermore, the obtained composite porous carbon possesses a much higher CH_4/N_2 separation coefficient (2.83) compared to the traditional activated carbon.

10.3 Towards Continue Manufacturing of Coal-Based Thin Films for Electronics, Sensing and Energy Storage

Nicola Ferralis, Jeffrey C. Grossman, MIT, USA.

Currently, synthetic materials showing the best performance for flexible electronics and soft robotics are often made from expensive feedstocks limiting their use at large industrial scale and at market competitive cost for both the feedstock and synthesis processes. The ultra-low cost of coal and its diverse chemical nature offers a wide range of exciting opportunities to be used as a "smart" material for thin films with tunable chemical, electric, mechanical properties. In this work, we propose a vertically integrated, processing method for deposition and property customization for the synthesis of electronic-grade thin films made of coal (neat or from derived products). We will show that through the use of scalable deposition methods, chemical functionalization and doping and localized thermal heating, electronic-grade thin films on flexible transparent substrates with tunable conductivity and transparency can be achieved. Furthermore, we will show that such ability to spatially control thermal annealing on the as-deposited coal-based film allows for the on-demand fabrication through direct “writing” of custom electronic devices. Performance of device prototypes of transparent joule heaters, and pressure-strain sensors fabricated on coal-based films on flexible substrates will be demonstrated. Ultimately, the ability to fabricate continuous coal-based films will enable the development of coal-based “smart” technologies, through the design of innovative yet inexpensive processes that are both compatible with continuous additive manufacturing, and flexible to allow on-demand on-film fabrication electronic devices, sensors and energy storage devices (such as ultracapacitors).

10.4 Brief Review of Thermal Graphitization of Coals and Carbons

Evan J. Granite, National Energy Technology Laboratory, USA.

The United States has the world’s largest coal reserves. Graphite and graphite-like materials can be interesting products from coal and other low-cost carbons. Coal forms from plant matter over geological time periods; i.e., millions to hundreds of millions of years. As the plant matter decomposes, the material becomes more ordered (coalified or graphitized) under the influence of time, temperature and pressure. Lower ranks of coal such as lignite are younger and contain less fixed carbon, visible plant material, more volatile matter and less ordered carbon. In contrast, high rank coals (anthracite) develop structures that resemble graphite. With the formation of high rank coals in nature as a starting point, this talk will briefly review thermal processes for the graphitization of coals and other carbon precursors.

10.5 Supercritical CO_2 Driven Production of Graphene and Aromatic Liquids for CNT

Kanchan Mondal, Southern Illinois University, USA.

The authors will discuss an early stage holistic process for the production of high value solid carbon materials, namely graphene quantum dots (GQDs) and aligned multiwalled nanotubes along with liquid fuels. GQDs are produced via a reductive route employing transfer hydrogenation of coal in supercritical CO2. It is a low temperature (<150 ºC) non-catalytic process using a hydrogen transfer agent (HTA) for direct coal liquefaction (CDL). The key idea behind the concept is that one hydrogen atom from water and one hydrogen atom from a hydrogen transfer agent (HTA) is used to hydrogenate the coal. Since the products of coal dissolution are non-polar and polar while the supercritical CO_2, that is used promote disruption the coal structure, enhance the rates of hydrogenation and dissolution of the non-polar molecules and removal from the reaction site, is non polar, a polar modifier (PM) for CO_2 was utilized to aid in the dissolution and removal of the polar components. In addition, to allow a seamless transport of the HTA and byproduct (oxidized HTA) between the aqueous and organic phases, a phase transfer agent (PTA) was added. Incidentally, the chosen PTA is also an effective phase transfer catalyst and aided the hydrogen addition and cleavage process. The results show that chemicals can be extracted from coal at temperatures ranging between 80 – 140 oC. Straight chain hydrocarbons for transportation fuels as well as chemicals that are needed as chemical precursors for commercial organics can be extracted from coal by this process. The amount of liquid produced was found to be enhanced if a coal structure disruption step is carried out before the coal hydrogenation step. This is achieved by the sudden expansion of the supercritical CO2. This step also resulted in the production of graphene quantum dots (GQDs) which are easily separated. Incidentally, the use of supercritical CO_2 not only provides high dissolution strength but also allows for easy separation of the chemicals from the solvent (normally gaseous under room conditions). We have shown that the aromatics and the heavy and light hydrocarbons can be separated by the pressure tuning the supercritical CO_2 at the exit. The monoaromatics are extracted from the co-produced liquids by modulating the pressure and temperature of the CO_2 leaving the reactor. The monoaromatics are used for the synthesis of aligned, long MWNTs by floating catalyst – chemical vapor deposition (FC-CVD). The remaining organic portion of the residue may be separated from the inorganic portion for fabrication of electrodes. We will present the findings from the evaluation of the process variables that establish the feasibility of the concept. Specifically, the effects of pressure, temperature and feed composition, the impact of a structure disruption stage on transfer hydrogenation of coal in supercritical CO2 and the effects of pressure, CO_2 soak time on the effectiveness of disruption on coal conversion will be presented along with the characterization of the products.

10.6 Investigations on Product Distribution and Oxygen Removal in the Newly Two-Stage Catalytic Lignite Liquefaction Process

Runze Zhao, Sheng Huang, Youqing Wu, Shiyong Wu, Jinsheng Gao, East China University of Science and Technology, CHINA.

Lignite is a promising feedstock for hydro-liquefaction as its abundant resources and high reactivity. However, its high oxygen and moisture contents limit its utilization in direct liquefaction due to the deoxygenation reaction that occurs during liquefaction in the presence of an iron-based catalyst consumes a large amount of hydrogen and produces water, resulting in a decrease in hydrogen partial pressure, further detrimental to hydro-liquefaction. In this paper, a newly two-stage catalytic lignite liquefaction process was proposed for optimizing the catalytic conditions in lignite liquefaction to obtain high conversion and oil yield. The first-stage lignite liquefaction was carried out in an autoclave at a temperature of 400 °C and a hydrogen pressure of 4 MPa, with the addition of Na2CO3. The second-stage lignite liquefaction was to sequentially hydrogenate the Na2CO3-treated lignite obtained in the first stage over FeOOH at a temperature of 450 °C and a hydrogen pressure of 4 MPa. Results showed that the proposed two-stage catalytic lignite liquefaction process could achieve higher conversion than a single liquefaction process, and significantly promote the conversion of preasphaltene and asphaltene to oil in lignite liquefaction. It was found that the first stage treatment over Na2CO3 presented a lower hydrogen consumption than that over FeOOH. The addition of Na2CO3 could effectively promote the cleavage of oxygen-containing groups and reduce the oxygen in the lignite structure. Through the two-stage liquefaction process, it can eliminate the adverse effects of large amount of water generated during the liquefaction of lignite on the macromolecular structure hydrogenation of lignite.

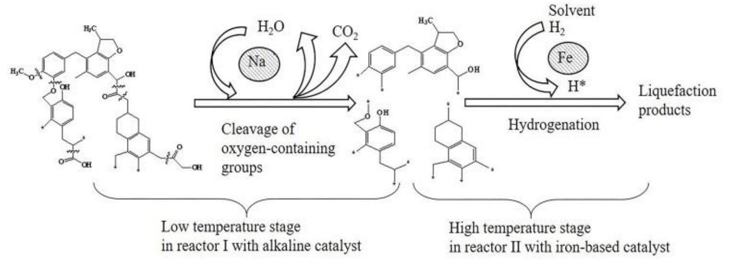

Figure 1. Schematic diagram of the proposed two-stage catalytic lignite liquefaction process.

SESSION 11
COAL ASH MANAGEMENT I
Tarunjit Butalia

11.1 Alternative Coal Ash Disposal Option for Stabilizing Ash and Wastewater for Power Plants and for Ash Relocation

Dale Timmons, NAES Corporation, USA.

Since the Effluent Limitations Guidelines (ELG) and Coal Combustion Residuals (CCR) rules were promulgated, the coal-fired power industry has been struggling with compliance requirements. Expensive compliance decisions are further complicated by the challenging economics and politics of producing power from coal. Many unlined ash impoundments have contaminated groundwater and some states have ordered unlined impoundments to be excavated and the ash relocated into more secure facilities. Beneficial reuse is a preferred option for this material, but markets are not large enough to recycle the vast amounts of ash and much of the ponded ash may not be suitable for recycling.

The Circumix Dense Slurry System (DSS) technology mixes wastewater with CCRs to produce a thick pumpable slurry to produce a solid, stable product with near-stoichiometric use of water. Once cured, the slurry exhibits low hydraulic conductivity, high compressional strength, no wastewater discharge, little or no fugitive dust and enhanced metals sequestration, thereby achieving the goals of the ELG and CCR rules. Although DSS has been used extensively in Europe and at one plant in the United States for decades, plant-specific testing is still required to establish the proper blend of solid waste products and wastewater for optimal environmental performance.

Ash-specific tests have shown that slight variations in the amount of water used to make the slurry can improve critical properties such as hydraulic conductivity and compressional strength of the cured product. These tests have also demonstrated that small quantities of additives, where indicated, can also dramatically improve product performance.

DSS is an economical alternative to traditional dry ash disposal and can be used to stabilize ponded ash subject to relocation. In addition to the advantages listed above, the cured product results in a solid surface suitable for redevelopment thereby reclaiming land that would otherwise be left unused for perpetuity.

The presentation will present power plant test data and case histories where DSS has been used to stabilize ash resulting in reclaimed and redeveloped land upon which new renewable power generation facilities have been established.

11.2 Stabilizing Wet Coal Ash: The Current State of the Practice

Greg Landry, Paul Schmall, Moretrench, A Keller Company, USA.

The most challenging part of ash basin closures is working on the highly unstable ash materials. The past several years have seen numerous applications of dewatering techniques in CCR which have been highly effective in improving the conditions for construction access and activities. Those techniques include rim ditching and sumping, wellpoints, deep wells, as well as horizontal methods.

Accessing the surface of any ash pond, even to install the dewatering system, still remains the initial challenge. Deeper ponds lend themselves to the use of widely spaced wells for dewatering, however, wells are typically installed with sizable drill rigs. Access has been facilitated with floating roads or a shallow crust created with wellpoint dewatering. With specialized methods, wellpoints are now commonly installed by hand from very wet and unstable pond surfaces. These wellpoints have been very effective for providing initial access to a pond for other construction activities.

Over the past several years we have learned to interpret geotechnical data to determine the best dewatering approach to stabilize a pond. Based on preliminary cone penetrometer (CPT) data, the target depth of penetration of the dewatering system can be anticipated. CPT data will provide some indication of the pond's hydrogeological behavior. Early field testing is typically performed to verify the hydrogeological behavior and depth of penetration of the dewatering devices. Pilot tests have been performed with shallow wellpoints and wells up to 150 feet in depth.

Advancements in dewatering techniques in CCR include high capacity well/wellpoint screen that is compatible with the difficult behavior of ash, the use of variable frequency driven pumps that are effective in very low yielding conditions and where the ash water chemistry is prone to well fouling.

This paper and presentation will include many case histories, widely varied applications and techniques, and lessons learned from work on over 20 ash basins.

11.3 Reducing Corrective Actions Through Modeling and Geochemistry

Ernie Stine, APTIM, USA.

Groundwater plume stability analysis (PSA) is a key process in the management and closure of coal combustion residue (CCR) sites and can minimize the extent of groundwater corrective/remedial actions. Groundwater at many CCR sites contains one or more of EPA Appendix IV metals. PSA can assess the extent and behavior of the metal plumes and determine if metals will migrate off site below regulatory criteria.

PSA includes data compilation and assessment, site conceptual modeling, geo- statistical evaluation, flow modeling and contaminant transport modeling. Typical statistical tools include Mann-Kendall analysis of non-parametric data, probability distribution functions, regression of concentrations versus time, and plume mass versus time. The use of these tools can determine if the plume size and mass are stable, increasing, or decreasing. For some sites, the statistical analysis and time-series concentration maps will help achieve site closure. However, more complex sites may require the use of 2-D or 3-D fate and transport modeling to demonstrate plume stability and establish compliance. If required, at some of these complex sites, a treatment train may include focused remedial action such as capping followed by monitored natural attenuation of the residual plume.

The paper presents examples of CCR sites where plume stability was established using the PSA and modeling procedures and natural attenuation was identified as the preferred pathway for site closure.

11.4 Applications of Environmental Risk Assessment in Coal Ash Management

Matt Huddleston, SynTerra Corporation, USA.

Environmental risk assessment has application in remediation and management of coal combustion residuals (CCR), commonly known as coal ash. CCR is created when coal is burned by power plants, and is a major industrial waste generated globally. In the United States, regulations for safe disposal of CCR are based on a culmination of extensive study on the effects of coal ash on the environment and public health. The county's "CCR rule" establishes technical requirements for CCR landfills and surface impoundments under the Resource Conservation Recovery Act (RCRA), the nation's primary law for regulating solid wastes. Coal ash can contain constituents that, if present in sufficient concentrations and certain forms, can pose risks to human health and wildlife if exposure occurs. Screening and "baseline" (quantitative) human health and ecological risk assessments were conducted for coal ash impoundments as part of comprehensive site evaluations for developing corrective action plans. Risk assessments followed federal, regional, and state protocols. Without the risk assessments, proposed remedies may have been based primarily on comparison of coal ash constituent concentrations to state groundwater and soil standards. Comparisons to regulatory standards alone often omit context and consideration of natural conditions, as well as introduce greater uncertainty associated with potential environmental risks. By implementing standard risk assessment procedures, in combination with groundwater modeling and site-specific conditions (e.g., geology, hydrogeology), utility owners and regulatory agencies can select the best remediation strategies to manage risks associated with CCR to acceptable levels.

11.5 Preparation of High Efficiency Potassium Calcium Silicate Fertilizer by Using the Fly Ash

Aiguo Chen, Xiaohuan Wang, Yongfeng Xiao, Huidong Liu, Xiaolin Jiang, Wenhua Li, National Institute of Clean-and-Low-Carbon Energy, CHINA.

China is in shortage of aluminum, nevertheless the aggregated demands for it are increasing yearly. For satisfying the needs of national economic development, the technologies of aluminum oxide extraction from fly ash were developed meanwhile importing a large amount of aluminum ore. One of these is known as one step acid-method fly ash aluminum oxide extraction process. The raw fly ash used for this process was from a power generation plant with CFD. Its main compositions were SiO2 and Al2O3. During the process, firstly the fly ash was immersed in acid solution at a certain temperature, and after reaction, the solved Al2O3 moved to next unit as solution, and the unsolved SiO2 named as "whit mud" was discharged as a residue. For this process, 1.35 ton of white mud was derived from when 1 ton of Al2O3 was produced. Environment friendly and valuable utilization of the white mud has occupied a very important portion for the wide commercial application of acid-method fly ash aluminum oxide extraction process.

By study and analysis of chemical, mineralogical, petrological and geochemical characteristics, some features of the white mud were revealed: 1) D50 of PSD was around 25.4 μm；2) observed by XRD its phase composition mainly was amorphous phase and crystalline phase, the diffraction peak formed bread shape in the interval of 20-30 degrees, indicated the amorphous phase was silica and unburned carbon, account for about 80%. The crystallization phase was mainly composed of anatase, quartz, rutile and mullite; 3) with highly enriched in SiO2, the concentrations of acid soluble elements such as Na, Al, Fe and some hazardous heavy metal elements were significantly lower than its raw fly ash; 4) about 60% of SiO2 in the white mud was with relatively high reaction activity, as the Al-extracting process broke down the Si-O-Al structure of amorphous phase of the fly ash, and partly performed the activation of silica in fact.

For the valuable utilization of the white mud, several production processes were investigated and studied including the production of white carbon black, molecular sieves, ultra-clear glass and so on. Based on the analysis both of technology and product market, the aim of this study was focused on the preparation of Potassium Calcium Silicate Fertilizer (PCSF). It has been proved that silicon is beneficial for the healthy growth and development of many plants, especially for gramineous plants such as rice, wheat, sugarcane and some cyperaceous plants. According to statistics, approximately 50% of the paddy rice soils in China are Si-deficient. Another function of silicon is it can passivate the heavy metal elements in soil that could be absorbed by plants.

The silicon that can be absorbed by plants is called the effective silicon. In order to transform the common silicon of white mud into the effective silicon, a roasting activation process was developed in this study. The research results have demonstrated that the selections of activation agents and ration, roasting temperature and time (90-150min) were the most important parameters for the preparation of high efficiency PCSF, and the carbon in the white mud and proper pelleting way were also beneficial to the activation of silicon. Under the condition of activation temperature 800-950°C and with the calcium and potassium or sodium as activating agents, the effective silicon content of the pelletized PCSF was as high as 26-34%, and the hazardous heavy metal (Cr Cd Pb Hg As) contents and pellet fertilizer（Φ3-5mm） hardness index were much satisfied with the related product standard requirements. By Six Sigma methodology, the regression equation of the effective silicon and activation agents, roasting temperature and time was created, and it complied well with test data.

SESSION 12
UNDERGROUND GASIFICATION
Harvey Goldstein and Rolf Maurer

12.1 Groundwater Monitoring During Mining of Coal In-Situ by Means of an Underground Coal Gasification Process

JC van Dyk, African Carbon Energy, North-West University; J Brand, African Carbon Energy; CA Strydom, FB Waanders, North-West University; South Africa.

Underground Coal Gasification (UCG) is a fast emerging, in-situ mining technology that has the advantage to access low cost energy through the utilization of coal reserves currently classified as not technically or economically accessible by conventional mining methods.

Groundwater monitoring in the South African mining industry for conventional coal mining is well established, with specific SANS, ASTM and ISO Standards dedicated for the specific environment, location and purposes. South-Africa's groundwater is a critical resource that provides environmental benefits and contributes to the well-being of the citizens and economic growth. Groundwater supplies the drinking water needs of large portions of the population and in some rural areas it represents the only source of water for domestic use. Utilization and implementation of groundwater monitoring standards are thus non-negotiable.

The groundwater quality management mission, according to the Department of Water and Sanitation in South-Africa, is set in the context of the water resources mission and reads as follows: *"To manage groundwater quality in an integrated and sustainable manner within the context of the National Water Resource Strategy and thereby to provide an adequate level of protection to groundwater resources and secure the supply of water of acceptable quality."[16]*

The scope in this paper is to propose fit-for-purpose groundwater monitoring standards for an Underground Coal Gasification commercial operation. It is important to pro-actively prevent or minimise potential impacts on groundwater through long-term protection and monitoring plans.

12.2 Evolution of Underground Coal Gasification

Burl E. Davis, Consultant, USA.

UCG technology has evolved from the Russian Linked Vertical Well configuration in the early 1970s to the linear and parallel CRIP systems now in development various locations around the world. The U.S. Department of Energy and its predeceasing agencies funded programs based upon the Russian program to utilize the vast coal resources in the United States. This program was enhanced by private industry efforts to bring the technology to commercial reality. This paper summarizes the path taken to bring the UCG process taken to bring the UCG technology to its present state. The author was a participant or an observer of many of these programs.

12.3 Diffusion Effect and Evolution of Kinetic Parameters During Coal Char-CO_2 Gasification

Dexi Meng, Xueli Chen, Tian Wang, Jianliang Xu, East China University of Science and Technology, CHINA.

Large coal char particle (LCC, 12 mm and 20 mm cube) and small coal char particle (SCC, less than 50 μm) were gasified under different temperatures in fixed bed reactor and thermo-gravimetric analyzer, respectively. The effectiveness factor and kinetic parameters (apparent activation energy and apparent pre-exponential factor) were also calculated to investigate the diffusion effect and the evolution of kinetic parameters during coal char-CO2 gasification. It was found that the internal effectiveness factor was not constant during the conversion process of coal char. In the intermediate and later stage of gasification reaction, there was a remarkable increase for the effectiveness factor. The effectiveness factor of LCC and SCC in the higher temperature range (1250-1400°C) were all much less than 1, which indicating that the gasification of LCC and SCC at high temperature was limited by pore diffusion. Apparent activation energy and apparent pre-exponential factor evolved continually throughout the conversion process, the existence of diffusion effect would lead to a certain change for the evolution law. A kinetic compensation effect was observed between the apparent activation energy and apparent pre-exponential factor during the conversion process of coal char. When the diffusion effect was very significant, it would have a certain weakening effect on the compensation effect.

12.4 CPFD Simulation on Particle Behavior in an Entrained-Flow Gasifier

Yongshi Liang, Cliff Y. Guo, National Institute of Clean-and-low-carbon Energy, CHINA.

A CPFD simulation model for entrained-flow gasification was established in this study. The simulation results agree with the experimental results. The detailed particle information and the particle residence time distribution were obtained by injecting particle tracers. The results show that the particles in the gasifier can be divided as three parts, i.e. a fast down-flowing part, a recirculation part and a general spread part. A criterion for this classification was also provided. The rapid gas expansion caused by the combustion plays a significant role in separating the particle stream into these tree parts. It accelerates the particles in the center of the gasifier while pushes the particles near the expansion edge into the gas recirculation. The particles in the fast down-flowing part directly flow through the high temperature region. Most of these particles were fully-reacted, although their residence times are the lowest. On the other hand, particles in the recirculation part have little access to the high temperature region. Most of these particles still have high carbon content although their residence times are the longest. Besides, the particles in the general spread part show moderate properties between the above two parts.

SESSION 13
RARE EARTH ELEMENTS I: RECOVERY OF RARE EARTHS I
Evan Granite and Fred McLaughlin

13.1 Rare Earth Elements and Critical Materials from Coal-Based Resources

Mary Anne Alvin, National Energy Technology Laboratory, USA.

Meeting and exceeding an extremely aggressive schedule for demonstrating production of dual use, high purity, rare earth elements (REEs) from coal-based materials, has occurred within the first five years of DOE-NETL's Feasibility of Recovering Rare Earth Elements Program. RD&D efforts are now focused on validating the potential for extracting, separating and recovering REEs in domestic, bench- and small pilot-scale, coal-based, REE-processing plants. This presentation provides an overview of the DOE-NETL REE program, and a summary of the technical accomplishments that have been achieved to date.

13.2 Adsorption of Critical Rare Earth Elements on ETS-10 Titanosilicate

Jay Thakkar, Blaine Wissler, Nick Dudenas, Xinyang Yin, Xueyi Zhang, The Pennsylvania State University, USA.

Rare Earth Elements (REEs) are essential in numerous modern technological applications. In the U.S., wastewater from coal mining and other mining activities is a new source of REEs. REEs exist in low concentrations and acidic conditions in mining wastewater. Recycling critically important REE cations – Y^{3+}, Dy^{3+}, Nd^{3+}, Tb^{3+}, and Eu^{3+} from aqueous waste solutions using porous inorganic frameworks e.g. zeolites has therefore gained significant attention. The present study evaluates ETS-10 (Engelhard Titanosilicate 10), a three-dimensional microporous member of the titanosilicates family, for adsorption and recovery of REE cations. ETS-10 has been extensively utilized for adsorbing heavy metals however, ion exchange of REEs on ETS-10 has not been studied before. By performing batch experiments in acidic aqueous solutions, it was found that ETS-10 is effective and has a high equilibrium adsorption capacity for these five critical REE cations. The adsorption strength of all five REE cations tested are significantly different ($Y^{3+}>Nd^{3+}>Eu^{3+}>Tb^{3+}>Dy^{3+}$). This indicates that ETS-10 is a suitable material for separating REEs from each other using membrane technology, such as membrane chromatography and ultrafiltration.

13.3 Recovery of Rare Earth Elements from Coal Seam Underclay

Scott N. Montross, LRST/National Energy Technology Laboratory; Circe A. Verba, US-DOE-NETL; Jon Yang, ORISE; Jinesh Jain, Sr., LRST/National Energy Technology Laboratory; Mark L. McKoy, US-DOE-NETL; USA.

Rare earth elements and yttrium (REY) are essential for the development of low-carbon, renewable energy technologies. Increasing demand from energy and high-end technology manufacturing sectors is currently bounded by a limited domestic supply of REY. To support the development of emerging renewable energy technologies, it is necessary to identify domestic sources of REY that are both reliable and economical. United States' domestic coal resources and coal utilization byproducts, including underclay and high-clay content mining wastes, are promising sources of recoverable REY. Multi-modal characterization techniques, including quantitative electron probe microanalysis (EPMA), were used to determine the elemental and mineralogical properties of the materials. Core flooding experiments were conducted to examine the efficacy of citric acid-based solutions for the extraction and recovery of REY from underclay samples using a selective, aqueous solution-based process to recover REY and other critical elements from the rock.

Preliminary results show the greatest concentrations of REY after the initial 20 minutes of continuous flow with rapidly decreasing concentrations afterwards. Increased recovery was achieved by saturating and holding in the solution at pressure before re-initializing flow. Continued flow after this increased hold-in time, however, showed rapidly decreasing concentrations after the initial 20 minutes of flow, suggesting a similar mechanism of REY recovery as before, but with potentially more time for solution infiltration into micro-pores and/or an effect of fluid residence times and 'saturation' states. The in-situ recovery and extraction efficiency for REE from geologic materials is heavily influenced by the permeation of extraction fluids into the rock matrix. Our process permits use of chelation compounds to keep mobilized REEs from easily re-adsorbing before being brought out of the source material or ore. The method can be applied to geological formations or other engineered waste products containing REY and other critical metals (e.g., Sc, Ni, Co). In-situ extraction techniques could be deployed wherever a REE-bearing layer is underlain by a layer with at least a modest permeability. In either at an open pit mine or an underground mine, the mine floor could serve as the leachate injection point or injection wells could be drilled and used for REE extraction in advance of mining. In-situ extraction of REE will drastically reduce costs by eliminating the need for grinding, crushing and conventional mining methods. Use of dilute leaching agents, transport mediators, concentrators, etc., commonly found in nature may reduce the environmental impacts and wastes, furthering reducing the life-cycle costs.

13.4 Low-Cost Methods for Rare Earth Elements Extraction and Recovery from Coal-Waste

Michael L. Free, Prashant K. Sarswat, Landon Allen, Aaron Noble, and Gerald Luttrell, University of Utah, USA.

Coal-based resources such as waste rock near the edges of coal seams often contain significant quantities of rare earth elements (REE). These resources are usually discarded in waste piles. These REE resources can be recovered through appropriate low-cost processing of the coal feed material to produce REEs. This low cost approach utilizes heap leaching with solutions from engineered biooxidation of pyrite naturally found with the coal resource, and the leached REEs are subsequently recovered through solvent extraction and precipitation. In order to address this opportunity for low cost REE extraction and recovery, the objectives of this study and the related DOE-funded project are to demonstrate and improve methods to economically extract, recover, and upgrade the rare earth element (REE) contents from vast coal-based resources using integrated modeling, targeted coal preparation, biooxidation, solution conditioning, heap leaching, solvent extraction, and precipitation technologies to produce REE-bearing products in an environmentally friendly way. Utilization of these integrated technologies will enable coal producers to utilize untapped resources to produce revenue and extend resource life while simultaneously reducing future environmental issues by removing or oxidizing pyrite prior to disposal. Although this approach is designed for existing coal ore processing facilities, it will be easily adapted in the future to the recovery of REEs and mitigation of acid rock drainage from coal tailings. Thus, this technology will enable recovery of an underutilized resource in an environmentally friendly way. Initial results from this study will be presented and discussed.

13.5 Rare Earth Elements in Acid Mine Drainage Precipitates: Results of A Regional Survey

Paul F. Ziemkiewicz, West Virginia University; Aaron Noble, Virginia Tech;
Chris Vass, West Virginia University; USA.

Acid mine drainage (AMD) is a longstanding environmental problem and has been studied extensively since the 1960s. While the process of AMD formation, control and treatment technologies are well understood1, its potential to supply critical materials, specifically REEs has been studied only recently. AMD is produced in vast quantities at both abandoned and current coal mining and preparation facilities. Coal producers are required to treat AMD to meet permitted water quality standards. Current AMD treatment is focused on meeting the pollution discharge limits imposed by the Clean Water Act: 33 U.S.C. §1251 et seq. (1972) for regulated, compliant water. AMD treatment consists of acid neutralization, mechanical or chemical oxidation and the settling of metal precipitates. Treatment systems remove metal contaminants as flocculated precipitates (flocs), which are then separated from discharge-quality water by either mechanical or gravitational settling methods. Known as AMD treatment precipitates or sludge, these metal flocs are enriched in REEs. Our earlier studies demonstrated that treatment of low pH AMD (< pH 5.5) produces a sludge with exceptionally high REE concentrations, often an order of magnitude greater than the surrounding rock strata.

AMD results from the oxidation of pyrite, a mineral common to the Appalachian region's coal measures. Pyrite oxidation generates sulfuric acid which leaches REEs from associated rock. During AMD treatment, REEs precipitate with the primary regulated metal ions of iron (Fe), aluminum (Al) and manganese (Mn) hydroxides.

AMD treatment systems are tailored to specific discharges and are designed to minimize capital and operating costs while meeting regulatory discharge standards. The resultant precipitates consist largely of Al, Fe and Mn oxy-hydroxides plus gypsum and carbonates. Iron is the dominant metal in strongly acidic AMD. Initially Fe occurs in its reduced (Fe^{2+}) state, oxidation to Fe^{3+} and precipitation as $Fe(OH)_3$ is nearly complete at pH 3.5 while Al^{3+} and Mn^{2+} hydroxides precipitate at pH values of 4.0 and 9.0, respectively. Prior results show that REEs precipitate along a pH gradient nearly identical to Fe^{3+} supporting the thesis REEs co-precipitate with the other metal cations. These metal hydroxide precipitates are collected in settling basins while treated water is decanted to surface discharge. Initially-formed AMD sludge is about 99% water. The solid fraction settles over time and depending on the treatment and storage process, may reach solids concentrations of 20 to 30%.

This project instituted a regional sampling effort that included an initial survey of sludge REE concentrations at a wide variety of AMD treatment sites. The results were used to identify sites with a high potential for REE recovery. A subset of this original population was selected for a second phase of intensive sampling to better determine variability within sites. The dominant factor controlling the Total REE (TREE) concentration in raw AMD is the pH of the raw water.

Findings of our regional sampling effort will be summarized including REE distributions, concentrations and the factors that influence grade of a given feedstock.

SESSION 14
CARBON MANAGEMENT I: PILOT DEMONSTRATIONS
Nick Siefert and Steve Carpenter

14.1 Ratemaking & New Technology: A Regulatory Innovative Approach to Carbon Capture Projects

Kara B. Fornstrom, Wyoming Public Service Commission, USA.

The carbon management table is a big one with many seats occupied by various interests promoting a common goal. The State of Wyoming is occupying several of these seats given its historic and economic reliance on coal production and coal fired electric generation. Wyoming's response to the downturn in the coal sector has been to lead.

Wyoming is leading in several ways. First, the Wyoming Legislature passed a suite of new laws about five years ago dealing with ownership of pore space, establishment of permit procedures for CCS sites and addressing liability issues, among others. Second, Wyoming is leading in technology innovation related to CCS and CCUS. Some examples include the creation of the Integrated Test Center (ITC) at Dry Forks Station (DFS) in Gillette which is hosting several tenants testing their CO2 utilization technologies at pilot scale. One tenant is the Carbon XPrize which has selected five finalists from India, China, Scotland and the United States to test technologies related to methanol, building materials, plastics and polymers. Other tenants include Membrane Technology & Research and Kawasaki Heavy Industries. In addition, the Wyoming CarbonSAFE project is led by the University of Wyoming with funding from the U.S. Department of Energy to study geologic CO2 storage in the vicinity of DFS. Third, Wyoming is leading the nation in an effort to reduce permitting burdens for new CO2 pipelines with the Wyoming Pipeline Corridor Initiative (WPCI); once completed, WPCI can serve as a model to facilitate CO2 pipeline development.

The purpose of this presentation is to pose the question: Is regulatory innovation the missing piece to promote CCUS development?

Regulated utilities control much of the global CO2 supply, yet most are not actively pursuing CCUS projects. In my view, there are two factors that are preventing them from "getting in the game". One, there is a significant difference in risk profile of those controlling this CO2 (regulated utilities), having a beta of .25, while their potential partners interested in developing enhanced oil recovery projects (exploration and production companies) have a beta of 1.5. The delta in risk profile makes it difficult to communicate and limits the ability to complete projects. Two, the traditional ratemaking model does not incentivize utilities to make investments in non-mature technologies, such as CCUS, in order to protect ratepayers from unnecessary cost. The lack of commercial success of CCUS projects make state commissions unlikely to approve cost recovery of infrastructure.

Earlier this year the Wyoming Legislature expanded the Wyoming Public Service Commission's innovative ratemaking jurisdiction which may lead to future policy decisions that would encourage participation in CCUS projects outside of rate base. Essentially, the Wyoming Legislature recognized that if a utility is to incur cost or risk not allowed into rate base, it should be allowed the opportunity to develop a separate revenue stream that is not included in annual calculation of return on rate base. Pursing these types of policies would encourage utilities to consider "out of the box" agreements with potential CCUS developers and allow them to share in the revenues generated by these projects. Ultimately, when CCUS project achieve commercial success, utilities would be more likely to have the opportunity to include significant capital investment into rate base. In an era of declining load, energy efficiency and distributed generation, the prospect of growing rate base is one that could encourage utilities to pursue CCUS.

While there are many seats at and conversations occurring at the carbon management table, I'd value the opportunity to convince attendees that one of those conversations needs to focus on innovative ratemaking to encourage regulated utilities to participate in CCUS projects.

14.2 Pilot Unit Testing of Alkalized Alumina Based Carbon Capture

Jeannine Elliott, Fei Yi, Brad Spatafore, TDA Research Inc., USA.

TDA Research, Inc. has developed a new CO_2 sorbent technology for post-combustion CO_2 capture from coal-fired power plants. This process is based on an alkalized alumina adsorbent that can remove CO_2 from flue gas of coal-fired power plants. We designed the process around its features to maximize the performance of the system. In our current work, TDA has built a 0.5 MW_e pilot-scale slipstream unit to test our sorbent-based post-combustion CO_2 removal system and demonstrate its technical and economic viability. The demonstration is being conducted at the National Carbon Capture Center (NCCC) in Wilsonville, AL. This project is funded by the DoE under Contract # DE-FE0012870. This work builds on previous bench-scale testing and a smaller demonstration on a coal derived flue gas at Western Research Institute.

This solid sorbent-based CO_2 capture has several features that make it unique. The alkalized alumina sorbent which removes CO_2 has a much lower heat of desorption than chemical absorbents, such as amine-based solvents. The process operates its adsorption and regeneration at around the same temperature. It operates nearly isothermally at ambient pressure. The sorbent is regenerated with low-pressure (inexpensive) steam without a temperature-swing or pressure-swing. Because of the isothermal operation it does not require heat recovery on the solids. To maximize capture efficiency and sorbent loading, it uses counter-current operation. The capture unit has 10 fixed beds that operate a simulated moving bed process. Each bed will switch between adsorption and regeneration processes, so that, at the same time, some beds are in the adsorption zone and the rest of the beds are in the regeneration zone.

TDA has completed construction of the ten-bed pilot unit and it is installed at the NCCC. The sorbent material was scaled up and loaded into the reactors. The 0.5 MW pilot unit test will demonstrate the CO_2 removal process on a real coal flue gas slip stream. Parametric and steady date testing of the pilot unit is planned to measure its performance under realistic long-term operation conditions. An update on the pilot unit results will be presented.

14.3 Pilot Testing of Amine-Based Solvent at Low-Rank Coal-Fired Power System

Jason D. Laumb, Principal Engineer, John P. Kay, David J. Dunham, Bruce C. Folkedahl, University of North Dakota, USA; Keisuke Iwakura, Tatsuya Tsujiuchi, Takashi Kamijo, Mitsubishi Heavy Industries, JAPAN; Tim Thomas, Mike Fowler, Osamu Miyamoto, Mitsubishi Heavy Industries America Inc., USA.

Carbon capture is being demonstrated at facilities in the United States, but unresolved challenges still need to be addressed with of sodium and sulfur content, ash content, NOx reduction, and footprint limitations. Fuel chemical makeup is crucial to the behavior of CO2 capture technologies that may be employed, whether from the buildup of heat-stable salts, aerosol formation, degradation of solvents, or subsequent solvent loss. The combustion of low-rank coals can produce aerosols that consist mainly of alkali and alkaline-earth sulfates as well as some minor and trace elements. These aerosols and trace elements have the potential to penetrate air pollution control devices and impact the performance of solvent-based CO2 capture systems. Testing at North Dakota lignite-fired power plants has found that the levels of aerosols on a number basis is on the order of 107 particles per cm^3 in the less than 100-nm range in the flue gas that would be routed to the CO2 capture system. This is in the range of 107–108/cm3 reported in literature for high emissions of solvent. Coal-fired combustion systems produce aerosols in the form of SO3 and alkali sulfates that form as a result of the condensation and reaction of flame-volatilized elements during gas cooling. Past testing conducted at the Energy & Environmental Research Center (EERC) has also shown that trace elements, including mercury, selenium, arsenic, lead, cadmium, antimony, and others, are vaporized during combustion. Most of the vaporized elements condense upon gas cooling and concentrate in the aerosol fraction of the ash. Many of these species, in addition to the problematic nature of aerosols on solvent emissions, have the potential to catalyze solvent degradation if they are allowed to build up in the solvent. Determination of the impact of degradation of the solvent and the economics of that degradation are unknowns at this point. Many of the elements that have been shown to catalyze solvent degradation are present in lignite coals and can exacerbate solvent replacement economics. The project team has conducted slipstream evaluations of Mitsubishi Heavy Industries, Ltd's proprietary KS-1™ solvent in order to address these potential challenges with low-rank fuel. Small pilot-scale testing was performed using the EERC's 0.05-MWe coal-fired combustor in conjunction with a 1-tonne/day catch-and-release CO2 capture system over 4 weeks utilizing both Powder River Basin and lignite coal. During lignite firing, the combustor was configured as a cyclone-fired system. Specific emphasis in this paper will be given to degradation, heat-stable salts, and aerosol formation. Sampling and testing were conducted to identify the presence of nitrite, nitrate, sulfate, thiosulfate, chloride, formate, acetate, and oxalate salts. Additionally, elements such as sodium, magnesium, potassium, mercury, and selenium were analyzed to determine if they are bound in the solvent. Sampling both upstream and downstream of the system was conducted to determine the presence of SO3 and aerosols.

14.4 Pilot Scale Testing of Hydrophobic Solvents for Precombustion CO_2 Capture

Nicholas Siefert, National Energy Technology Laboratory, Carnegie Mellon University; Wei Shi, Robert Thompson, David Hopkinson, National Energy Technology Laboratory; Michael Swanson, Joshua Stanislowski, University of North Dakota Energy and Environmental Research Center, USA.

The National Energy Technology Laboratory's Research and Innovation Center (NETL/RIC) has developed two new pre-combustion solvents exhibited improved carbon dioxide (CO2) capture performance at 40°C than two commercially-available solvents at 10°C during pilot testing downstream of a fluidized bed gasifier. The baseline solvent for precombustion CO2 capture in NETL's IGCC-CCS Bituminous Baseline Report [1] is Selexol® (UOP LLC), a hydrophilic solvent that readily adsorbs water, which unfortunately lowers the CO2 loading and increases the viscosity. NETL has developed solvents that are more hydrophobic than Selexol and more selective for CO2 over H2 at higher absorption temperatures. We aim to improve the efficiency of IGCC-CCS power plants by capturing CO2 at or above room temperatures in order to eliminate chillers/coolers and to regenerate the solvent using waste heat.

The two NETL developed low-cost, hydrophobic solvents are labelled PEG-PDMS-3 and CASSH-1. PEG-PDMS-3 was developed and synthesized within RIC in order to derive the advantages of both PEG and PDMS chains [2]. CASSH-1 was chosen using an in-house computational screen technique in which ~23,000 solvents were screened and down-selected based on their physical properties. Some properties of the solvents, such as vapor pressure and solvent viscosity at 25 [Symbol]C, were determined using the NIST database, and some properties of the solvents, such as CO2 and H2 uptake, were estimated from molecular modeling and by using databases created in-house by NETL/RIC. CASSH-1 was predicted to be the best performing of the original ~23,000 solvents.

The two NETL solvents, along with a Selexol surrogate (Coastal Chemical Co. LLC, AGRII) and also with tributyl phosphate (TBP), were tested in a packed-bed absorber following a fluidized bed coal gasifier at the University of North Dakota's Energy and Environmental Research Center (UND EERC). The two NETL developed solvents had higher CO2 uptake and higher CO2/H2 selectivity at 40°C than even the baseline solvent had at 10°C. Crucially, these NETL solvents can capture more CO2 and less H2 without having to chill the solvent. In this presentation, we will present experimental results from the pilot-scale testing and we will compare these results with simulations of the absorption process in Aspen Plus.

14.5 Initial Testing and Technology Update from the Wyoming Integrated Test Center

William James Morris, Wyoming Integrated Test Center; Jason Begger, Wyoming Infrastructure Authority, USA.

The state of Wyoming completed construction of a world class integrated test center (ITC) for evaluating post combustion CO2 capture technologies in 2018. An asset of the Wyoming Infrastructure Authority, (WIA) with additional funding and support from Tri-State Generation and Transmission, Basin Electric Power Cooperative, and the National Rural Electrical Cooperative Association, the center features over 20 MW equivalent (MWe) of coal derived flue gas from the adjacent Dry Fork Power Station in Gillette, WY, USA.

The Dry Fork Station, operated by Basin Electric Cooperative, is a state-of-the-art plant with best available NOX and SO_2 control technology providing reliable low emissions flue gas to the test center. The plant utilizes coal from the adjacent Dry Fork mine in the Powder River Basin. Approximately 2-2.5 MWe is provided to 6 small test bays of 0.4 MWe each which may be operated concurrently or independently. The test bays utilize a flue gas system with recirculation fans allowing any one of the test bays to come online or shut down without disrupting the flue gas supply or operations of any of the other test bays. The large bay, which can provide approximately 18 MWe of flue gas, and small test center bays are also able to operate independently of one another. Each test bay is provided with its own flue gas, power, and water supply. The test bays are located in a secure area adjacent to the plant to allow researchers to operate independently of plant operations.

The small-scale test bays are hosting the international NRG COSIA Carbon XPRIZE CO2 capture and conversion/utilization competition (coal track). In addition, one test bay will also be the host site for the Kawasaki Heavy Industries' Carbon Capture Process using a dry adsorbent and low regeneration temperature. An additional technology developer, TDA Research, will commission a hybrid membrane and solid adsorbent capture technology Q2 or Q3, 2019. An update on progress will be presented. Additional testing programs are being negotiated and updates will be presented regarding additional testing campaigns.

The large pilot test bay can provide 18 to 20 MWe of flue gas for a single technology test or be further subdivided to host multiple technologies at greater than 1 MWe scale. The ITC has supported two phase 2 applications for the U.S. Department of Energy funding opportunity announcement DE-FE0031587. The applicants, the University of Kentucky and Membrane Technology and Research (MTR) are proposing novel second-generation capture systems capable of capturing ~200 tons per day of CO2. The University of Kentucky will utilize a solvent approach with advanced system design while MTR will utilize their membrane module system.

While the ITC is currently working with projects funded privately through the XPRIZE competition, the Japanese Ministry of Environment, and the U.S. Department of Energy and National Energy Technology Laboratory, ITC is open to individuals, companies, and research organizations who have the capability to conduct self-sustained CO2 capture testing from an operating coal fired power station. The ITC is also located adjacent to the University of Wyoming's CarbonSAFE injection and monitoring site as well as within 10 miles of an existing CO2 pipeline for enhanced oil recovery which uniquely positions the ITC as a hub for CCUS research opportunities.

Wyoming's ITC is serving as a catalyst for aligning Wyoming's efforts for research, testing, pre-commercialization, and commercialization of CCUS technologies.

SESSION 15
COAL MINING, PREPARATION AND HANDLING
Richard Winschel and Daniel Connell

15.1 The Omnis Separation Plant; Transforming Coal Waste into High-Value Products

Greg Smith, Omnis Energy, USA.

Over 70% of the world's topsoil has been lost in the last 150 years and demand for clean, low-cost energy is exponentially increasing. With the World's population forecasted to reach 9.6 million by 2050, energy and food security is one of the world's greatest challenges.

Omnis Energy have developed a technology to transform coal waste into high-grade energy and agricultural products to meet this challenge. The Omnis Separation Plant cost-effectively separates coal waste, from both underflows generated by ongoing operations and waste sites subject to reclamation, into ultrafine carbon, mineral and water fractions. This facilitates the production of ultra-pure carbon products for energy and industrial markets in addition to a mineral product that can be used to restructure and rebalance damaged soil, revitalizing farmland and boosting plant growth.

Patented milling, micro-particle separation and dewatering process steps are incorporated into this process and products can be engineered to meet customer and logistical needs. Through the utilization of coal waste as a feedstock, Omnis Energy is also addressing the environmental and financial liabilities associated with coal waste for past, current and future land users.

Following several years of laboratory and pilot-scale research and development, including successful trials conducted by purchasers, the first plant in the United States is currently under construction at CONSOL's Bailey operation in Pennsylvania. Additional plants are also being constructed in China through Fenix Technologies, a "sister" company to Omnis Energy.

15.2 Opportunities to Advance Coal through "Upstream" Technology Development in Mining and Beneficiation

Daniel P. Connell, CONSOL Energy Inc., USA.

Coal remains a vital source of energy in the United States and around the globe, accounting for about 27% of U.S. electricity generation and providing 58% of the primary energy consumed by China and India in 2018. As such, the U.S. holds substantial value in its vast proven coal reserve base, which is the largest of any country in the world. However, in order for this value to be fully realized, new technology development for "upstream" aspects of coal – including mining and beneficiation – is needed in order to keep coal competitive with rapidly evolving energy sources such as natural gas and renewables. While substantial federal R&D spending has been directed toward controlling emissions from coal combustion and improving the efficiency of coal-fired power plants, relatively little has been invested in upstream portions of the coal supply chain even though these factors prominently in the overall value proposition for coal as well. The cost of the coal feedstock is a major factor in determining the competitiveness of domestic coal-fired power plants, U.S. coal exports, and non-power end-uses of coal, and coal mining, processing, and transport factor prominently in coal's overall environmental, health, and safety profile. This presentation highlights new technology opportunities in coal mining and beneficiation – including opportunities in the areas of automation and robotics, big data and advanced computing, fully remote mining, waste coal recovery and utilization, and new product streams – and discusses potential implications for the coal industry.

15.3 Study on Fluidization Characteristics of Geldart D Particles Based on Analysis of Impact Force in a Vibrated Gas-Fluidized Bed

Song Wang, Liang Dong, Bo Zhang, Yuemin Zhao, Xuliang Yang, China University of Mining and Technology, CHINA.

Coal preparation can effectively remove impurities in raw coal, reduce the content of ash and sulfur in coal to improve coal quality and reduce environmental pollution. The purpose of this paper is to solve the difficult problems in the process of fine coal separation in a vibrated gas-fluidized bed (VGFB). The fluidization characteristics of binary Geldart D type particles in a VGFB were studied deploying the measurement by impact force sensor system. The synergistic effects of the operational parameters including vibration amplitude (A), vibration frequency (f) and fluidizing air velocity (U) on the fluidization characteristics of a VGFB were studied. The results showed that the fluctuation range of the signals of pressure drop and particulate impact force decreases with the increase of fluidizing air velocity and bed height due to the energy dissipation of vibration and the increase of bed expansion ratio. Furthermore, the effects of bubbling behavior on the pressure drop and particulate impact force were revealed by the combination of the frequency domain analysis of signals. The result show that the separation process in a VGFB has good effect on separation under vibration conditions (A = 2 mm, f = 25Hz) of Geldart D type particles, which were used as substitutes for fine coal. The slugging behavior is also appeared when the gas velocity U = 112 cm/s, which is beneficial to separation, and is verified by high-speed dynamic image.

15.4 Modelling New Scheme on Coal Procurement for Coal-Fired Power Plants in Indonesia

Firly R. Baskoro, Keisuke Nagasawa, Katsumi Morikawa, Katsuhiko Takahashi, Hiroshima University, JAPAN.

Indonesia is blessed with relatively abundant coal resource and reserve in comparison to other fossil fuels resource. The latest data in 2018 from the Ministry of Energy and Mineral Resources of the Republic of Indonesia shows that Indonesia has 128,062.64 million tons of coal resource and 28,457.30 million tons of coal reserve. Currently, coal in the domestic market mostly utilized for the electricity generation which principally generated by using coal-fired power plant. In the last 2018, the Indonesian government announced the 35,000 MW project for additional capacity of electricity generation, which results in additional installment for over 20,000 MW of coalfired power plants. The electricity generation in Indonesia is conducted under the supervisory of the state-owned electricity company (Perusahaan Listrik Negara – PLN). However, the procurement system for coal as a raw material for coal-fired power plant is conducted individually by each unit of power plants without considering the needs of other units in other locations, by using traditional direct supply method from the supplier's jetty to the coal-fired power plant's port. As a consequence, only a limited number of candidates that can be successfully selected as a supplier. This current procurement system will raise a problem in terms of the availability of coal reserve in Indonesia, which directly affects the security and continuity of supply issues. As an archipelago country, Indonesia consists of many islands which will increase the complexity of coal distribution from the supplier to the coal-fired power plants. Therefore, this study will be carried out to analyze the advantages of the new scheme of coal procurement. In this proposed new scheme, both the integration and zonation of coal procurement mechanism for all units will be taken into account. The optimization will be conducted by considering the power plants' requirement, coal specifications, port capacity, and available facility for coal transportation. Mixed-integer linear programming will be introduced as the method for the problem-solving. As the results, the proposed new scheme will be the best option in minimizing coal procurement cost, while also maximizing the utilization of coal in the domestic market.

15.5 Coal Dust Treatment Technology for Coking Coal Moisture Control

Hamyung Jeong, JeaHoon Choi, POSCO, SOUTH KOREA.

Coal drying technology has been used to increase the charging density of coal in coke ovens. Generally, the less coal moisture, the more dust emission. This can be an obstacle to the operation, so the coal dust treatment is one of the most important technology for stable operation. In this study, the characteristics of coal dust with water and BET (Biological Effluent Treatment) sludge were analyzed. As the moisture content of coal dust changed (2.9% -> 9.4%), the angle of repose and average grain size increased and the charging density (744kg / m3-> 582kg / m3) decreased linearly. As the moisture content in the coal dust increased, the fine fraction less than 0.15mm gradually decreased and the compressive rate increased linearly. Coal Dust, which occurs during coal drying, is not easy to mix even if water is added because of loss of hydrophilicity. By using BET sludge, the coal dust can be effectively mixed, and this can improve the fluidity of the granule.

15.6 Influence of Gas Compressibility on a Burning Accident in an Obstructed Coalmining Passage

Furkan Kodakoglu, V'yacheslav Akkerman, West Virginia University; Sinan Demir, Georgia Institute of Technology; USA.

Historically, accidental gas and dust explosions have constituted a hazard to both personnel and equipment in the coalmining industry. The modern knowledgebase still does not provide an acceptable level of risk. Therefore, a novel preventive mining/fire safety strategy is critically needed, which requires a rigorous predictive scenario of a mining accident. A step towards such a predictive model was recently undertaken by the joint team of researchers from West Virginia University (WVU) and Worcester Polytechnic Institute (WPI). The WVU-WPI model assumed smooth walls of a mining passage. However, it was subsequently recognized that obstructions, which are inevitably present in a mine (such as mining equipment, conveyor belt systems, and piles of rubble), may block a noticeable part of a passage, thereby providing a significant impact on the fire dynamics. In the present work, we overcome such a shortcoming by incorporating the obstacles into the predictive model of the coalmining fire scenario. For this purpose, the theories of globally-spherical, self-accelerating premixed expanding flames, finger flame acceleration, and ultrafast flame acceleration in obstructed conduits are combined into a novel, unified analytical formulation. Specifically, we have identified and scrutinized the key stages of the premixed flame front evolution and quantified its major characteristics such as the flame tip position, its velocity, acceleration rate, and the run-up distance. Starting with gaseous burning, the formulation is subsequently extended to a gaseous-dusty environment with combustible (coal) and inert (sand) dusts and their combination considered. Specifically, the impacts of the equivalence ratio, dust size, and concentration on the flame evolution are systematically studied. Both two-dimensional and cylindrical-axisymmetric geometries for a mining passage are employed and compared, with stronger acceleration found in the cylindrical case. It is shown that the entire acceleration scenario may promote the flame propagation velocity up to a near-sonic value, forming a potential of detonation triggering by an accelerating flame. Starting with an incompressible approach, in this particular work we extend the analysis to account for gas compressibility, because the latter cannot be ignored as soon as the flame velocity starts approaching the sound speed. This is the focus of the present work. It is shown that gas compressibility generally moderates flame acceleration, and such an impact depends strongly on various thermal-chemical properties of the mixture. In particular, the role of compressibility is relatively small for very fuel-lean and fuel-rich flames, thereby justifying an applicability of the incompressible formulation in those cases. In contrast, compressibility appears to have a crucial importance for a near-stoichiometric combustion, thereby making the present analysis essential.

SESSION 16
COAL ASH MANAGEMENT II
Tarunjit Butalia

16.1 The Innovative Process of Harvesting Fly Ash from a Closed Pennsylvania Landfill for Beneficial Use

Angie Gerdeman, Hull & Associates; Ivan Diaz Loya, Boral CM Services LLC; Farshad Rajabipour, Penn State University; Tarunjit Butalia, The Ohio State University; William Petruzzi, Hull & Associates, Inc.; USA.

To prepare for an increased demand for fly ash in concrete-related infrastructure projects, proactive facility managers and ash brokers can now harvest fly ash from active and inactive storage areas. Innovative and successful material harvesting efforts were recently completed at a closed 30-acre fly ash landfill in Pennsylvania. Within just over three years, the project team completed initial feasibility analyses; planning; detailed material characterization; thorough evaluations of the existing facility and infrastructure; detailed design, phasing and construction drawings; and construction and certification of new surface water and contact water management structures needed during harvesting operations. This site started producing harvested concrete-grade fly ash in the spring of 2019 and required a flexible and adaptive approach to address approval requirement changes and historic adverse weather conditions.

Harvesting materials previously considered a waste product in a regulated facility presents many engineering and regulatory challenges and precedents. Identifying the need for program guidance related to this new service area, and using this Pennsylvania project as a case study, project team members served on a E50.03 Subcommittee within the ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action to prepare the new ASTM Standard Guide for Harvesting Coal Combustion Products Stored in Active and Inactive Storage Areas (ASTM E3183). Panel presenters will provide an overview of fly ash use in concrete; share the current state of supply and motivation to harvesting; provide the potential benefits and challenges to using landfilled fly ash in concrete; present a statistical sampling plan for evaluating landfilled fly ash beneficial use; share details of facility approval activities; discuss critical steps necessary for project success; provide lessons learned that will be useful for future beneficial use projects; and share site-specific examples to help introduce and explain concepts from the new ASTM Guide. The panel presenters will be as follows:

Speaker 1: Dr. Ivan Diaz Loya Dr. Ivan Diaz Loya is Director of Research at Boral Resources, Taylorsville, GA. He holds a PhD in engineering from Louisiana Tech University and has more than 10 years of experience in fly ash research. He is a member of ACI Committees 232, Fly Ash in Concrete; 240, Natural Pozzolans and 236, Material Science of Concrete. He is also a member of ASTM Committees C 01 on Cement and C09 on Concrete and Aggregates. His research interests include fly ash reactivity in concrete, alternative supplementary cementitious materials and identifying and developing processes to beneficially use coal combustion products. This part of the presentation will provide an overview of fly ash use in concrete, mainly focusing on its effects in fresh and hardened concrete. The presentation will also cover the current state of supply and motivation to harvest from the utility side.

Speaker 2: Dr. Farshad Rajabipour Dr. Farshad Rajabipour is an Associate Professor of Civil Engineering at Penn State. He is also the Associate Director for USDOT's Center for Integrated Asset Management of Multi-modal Transportation Infrastructure Systems. He earned a B.Sc. degree from Sharif University of Technology and M.Sc. and Ph.D. degrees from Purdue University, all in Civil Engineering. He has 18 years of teaching and research experience in support of sustainable civil infrastructures that are safe, durable, reliable, cost effective, and environmentally positive. Specifically, he performs research on concrete durability and life extension, unconventional pozzolans, lowCO2 cements, bridge preservation and asset management, and automated construction using additive manufacturing. This part of the presentation will provide a summary of the potential benefits and challenges associated with using landfilled fly ash in concrete. In addition, it presents a statistical sampling plan for reliable evaluation of the quality and uniformity of fly ash within a given landfill, and for determining the necessary beneficiation steps that must be applied to landfilled fly ash.

Speaker 3: Angela Gerdeman Angela Gerdeman is a Senior Project Manager and the Landfill Engineering Practice Leader at Hull & Associates, Inc. in Toledo, Ohio. Angie has a Bachelor of Science degree in Civil Engineering from the University of Toledo and is a registered professional engineer in seven states. She serves on The University of Toledo Department of Civil Engineering Industrial Advisory Board and was one of the primary authors of ASTM E3183, a Standard Guide for Harvesting Coal Combustion Products Stored in Active and Inactive Storage Areas for Beneficial Use. She has 30 years of civil and environmental engineering experience including the siting, design, permitting, construction quality control/quality assurance, operational planning and phasing, compliance, and closure/post-closure of municipal, industrial, residual, and construction and demolition debris landfills. This part of the presentation will provide a summary of the engineering aspects of the closed landfill ash harvesting project including the evaluation of the existing facility and infrastructure; detailed design and phasing; regulatory approval process; and construction and certification of the new engineering controls needed for harvesting. This will also include critical steps necessary for project success, provide lessons learned that will be useful for future beneficial use projects, and share site-specific examples to help introduce and explain concepts from the new ASTM Guide.

Panel Concept
The diverse panel will provide perspectives from industry, academia and consulting. The panel will be co-moderated by Dr. Tarunjit Butalia and William Petruzzi.

SESSION 17
PYROLYSIS I
Diane Revay Madden and Francis Lau

17.1 Development of Internal Surface Area During Pyrolysis and Gasification of Low-Rank Coals

Sittichai Natesakhawat, Evan Granite, National Energy Technology Laboratory, USA.

There have been numerous studies of both the thermal reactions and use of coals to make inexpensive activated carbons [1-9]. The development of internal surface area during the pyrolysis and gasification of powdered lignite and subbituminous coals was studied by using a small flow reactor and a thermal gravimetric analyzer (TGA). The BET surface areas, total pore volume, and average pore diameters of the chars formed were determined. The results have significant implications with respect to gasification and combustion of coals. Impressive surface areas were obtained by treating the coals with simple and non-optimized procedures. The simple methods employed in this study may also suggest means for forming inexpensive activated carbons from abundant domestic coals.

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17.2 Gasification Characteristics and Kinetics Analysis of Rapid Co-Pyrolysis Char from Lignite and Cotton Straw

Qing He, Guangsuo Yu, Qinghua Guo, Juntao Wei, Jianliang Xu, Yifei Wang, East China University of Science and Technology, CHINA.

Co-gasification of biomass and coal can alleviate the contradiction between energy demand and environmental protection. The gasification of carbonaceous materials usually includes the generation of pyrolysis char and char gasification. Char gasification is the control step. In present work, cotton straw (CS) and Hongshaquan lignite (HSQ) were selected as experimental materials and high frequency furnace was used to produce the rapid co-pyrolysis char. The crystal structure, specific surface area and ion-exchanged alkali and alkaline earth metals (AAEM) of co-pyrolysis char were analyzed. Isothermal gasification and non-isothermal gasification were carried out by thermogravimetric analyzer (TGA), respectively. It was found that more K elements appeared on the surface of coal char, and the amorphous carbon structure of coal char increased after rapid co-pyrolysis. The specific surface area of the mixtures was greater than the calculated average value. CS contained more volatiles and the H radicals generated during rapid pyrolysis reacted with coal, which improved the yield of H2 and also expanded the pore surface area. In addition, AAEM released from biomass would load on the coal char and resulted in pore enlargement. Isothermal gasification and non-isothermal gasification had different reaction characteristics. As for non-isothermal gasification, the reaction rate had only one peak and the maximum reaction rate of the mixtures was increased. As for isothermal gasification, the reactivity of co-pyrolysis char was inhibited in the early stage and was promoted in the late stage according to synergistic factor. The inhibition effect was consistent with the decrease of the ion-exchanged AAEM. The synergistic effect of co-gasification was related to AAEM migration and transformation. Besides, the activation energies (Ea) of gasification were calculated by Coats-Redfern method and model-free method, respectively. The Ea of non-isothermal gasification was greater than that of isothermal gasification. Ea of CS char was about 0.6 times of that of HSQ char for both non-isothermal and isothermal gasification. And the Ea of the mixtures had a good linear correlation with the mass ratio of the char.

17.3 Hydrogen Balance for Co-Pyrolysis of Lignite and Different Hydrogen-Rich Additions

Yanling Li, Sheng Huang, Youqing Wu, Shiyong Wu, Jinsheng Gao, East China University of Science and Technology, CHINA.

In this study, rice husk (RH) and Petroleum residue (PR) were used to co-pyrolyze with Xilinhot lignite (XL), respectively, in an an aluminum retort at a low temperature of 550 ºC. The experimental yields of co-pyrolysis products were comapared with calculated values, and 1Hydrogen-nuclear magnetic resonance (1H-NMR) and Gas chromatography-Mass Spectrometer (GC/MS) analysis of individual pyrolysis and co-pyrolysis tars were carried out to investigate the hydrogen transfer route and the potential interaction mechanism between feedstocks. Results indicate that co-pyrolysis of RH and XL exhibits more water and less tar than expected. The tar molecules from co-pyrolysis are with shorter side-chains, which may be because that more methoxyl free radicals from RH transfer into XL derived tar than individual pyrolysis. For co-pyrolysis of PR and XL, compared with calculated values, less water, more gas and slightly more tar are obtained. And the relative contents of Hβ (aliphatic hydrogen on Cβ and the CH2, CH beyond the Cβ to aromatic rings) and Hγ (aliphatic hydrogen on Cγ and the CH3 beyond the Cγ to aromatic rings) in PR and XL co-pyrolysis tar are extremely higher than expected.

17.4 Study on Lignin Pyrolysis Based on IT-PY-GC/MS/SIM

Fuxin Chen, Junxing Zhang, Feiyang Duan, Anning Zhou, Xian University of Science and Technoloty, CHINA.

Isotope tracer method (IT) is the use of radioactive nuclides as a tracer to tag the research object of trace analysis method. Pyrolysis- Gas Chromatography-Mass Spectrometer is a powerful tool for biomass or coal research. In this study, deuterium, oxygen 18 and carbon 13 are used as tracer, and MS system is used for testing. In addition, the contents of isotopic products are low abundance and the rate of isotopic exchange reaction is also indeterminate, so, the use of selective ion scanning mode (SIM) of isotopes replace under the same retention time and the replace the pyrolysis products would be better. More concretely, 1.00 mg lignin powder and 5μL H2O (including tracer in pyrolysis small cup respectively); pyrolysis condition were set temperature of 250 ℃ and the pyrolysis time 1 min; Full scan mode (TIC) chromatograms of retention time and the integral area were obtained by Agilent ChemStation automatically, using qualitative chromatographic peak NIST08 spectral library. For phenol, 2-methoxy-1-vinyl-phenol, 2,6-dimethoxy phenol, 2,6-dimethoxy-4-allyl-phenol, these four compounds were selected for the mechanism research. Results show that compared with phenol, the relative content of O18-D-phenol is up to 34 times under copyrolysis of lignin and 5μL H2O (including D2O in the pyrolysis products of the total),. This result also suggests that, the concentration of hydrogen radical is much higher than hydroxyl free radical under pyrolysis reaction, and about 21 times for influence.

17.5 Integrated Low Carbon Alkanes Activation with Coal Pyrolysis for Improving Coal Tar Yield,

Haoquan Hu, Lijun Jin, Yang Li, Dalian University of Technology, CHINA.

Pyrolysis is an efficient approach for coal clean utilization. It is considered that the coal pyrolysis is radical reaction, and the manner of free radicals' stabilization will determine the product distribution. To improve the tar yield in coal pyrolysis, several processes to integrate catalytic and/or low-temperature plasma activation of methane (including partial oxidation, CO_2 reforming, steam reforming, methane aromatization and cold plasmas) and ethane (including CO2 reforming and steam reforming) with coal pyrolysis were conducted. The results showed that all integrated processes can obviously improve tar yield compared with the pyrolysis under N_2 or H_2 and are adaptable to different coals. These methods provide new approaches for enhancing the tar yield. The mechanism for high tar yield was analyzed by the isotopic trace techniques. The analysis of main components in the tar from the integrated process by GC-MS indicates that some free radicals (like [Symbol]CHx, [Symbol]H) are formed by the catalytic activation of methane on Ni-based catalysts or the excitation by electrons with higher energy in low-temperature plasma. These active species participate in the formation of coal tar by the interaction with the free radicals cracked from coal, leading to the remarkable enhancement. The isotope trace experiments of integrated process of coal pyrolysis with steam reforming of ethane with deuterium oxide (D2O) and deuterated ethane (C2D6) also show that D2O and C2D6 contribute to coal tar formation in the form of activated free radicals including[Symbol]D, [Symbol]CD3 and [Symbol]C2D5, etc. The reactor designing of the integrated process and the catalyst development with good catalytic performances for methane and ethane activation are the key to the industrial utilization in the future.

SESSION 18
RARE EARTH ELEMENTS II: CHARACTERISATION AND ANALYTICAL METHODS OF RARE EARTHS
Mary Anne Alvin and Evan Granite

18.1 Using Yttrium as an Indicator to Estimate Total Rare Earth Element Concentration: A Case Study on the Rare Earth Element Distribution Patterns of Coal-associated Clays from Eastern Pennsylvania

Xiaojing Yang, Daniel Kozar, The Pennsylvania State University; Daniel Gorski, Anthony Marchese, Texas Minerals Resource Corporation; James Pagnotti, Pagnotti Enterprises; Rusty Sutterlin, Inventure Renewables, Inc.; Mohammad Rezaee, Mark S. Klima, Sarma V. Pisupati, The Pennsylvania State University; USA.

For any profitable commercial rare earths or critical minerals project identification of resource with high Assay is very important. This study explored and developed a refined correlation using yttrium (Y) as an indicator to estimate the total rare earth element and yttrium content (REY) in coal-associated clays and to facilitate selection of samples with high REY assays. More than 10 coal associated samples were collected from each of three anthracite coal mining sites from eastern Pennsylvania based on the gamma-ray logs indicating potential high REE content (Sites B, J and C). Several samples from each site were analyzed by ICP-MS to determine the rare earth distribution patterns and to establish the site-specific linear equation of Y and REY. The Y contents of the remaining samples were measured by a field XRF analyzer that could be operated in the field or onsite lab, and the REY values were calculated. R-squared values above 0.70 were obtained for all the estimation equations from all three sites on both a whole sample basis and an ash basis. The ash contents of site B were highly associated with REY, so using ash content would result in a more accurate estimation than using Y. However, in the case of site J where ash contents could not be correlated with REY, this method was more applicable. This estimation process is suitable for small samples sizes (<10) (site B and J) that share more homogeneous distribution patterns as well as larger sample sizes (>30) that share various distribution patterns (site C). In addition, compared to using the traditional ICP measurements for all samples, using XRF for the majority of the samples can significantly reduce the time and cost required especially for large quantities of samples, resulting in a faster and less expensive selection process.

18.2 Microanalytical Characterization of Rare Earth Elements in Coal-associated Clays

Circe Verba, US-DOE-NETL; Jon Yang, ORISE; Scott Montross, LRST/National Energy Technology Laboratory; Christina Lopano, US-DOE-NETL; Mengling Stuckman, LRST/National Energy Technology Laboratory; Mark L. McKoy, US-DOE-NETL; USA.

With the critical importance and high demand of rare earth elements (REEs) in technological applications, identifying novel resources of these elements is becoming increasingly important in a market constrained by limited domestic production. In the U.S., opportunities exist to explore potential REE extraction in coal waste streams and coal-related strata; early studies have demonstrated promising resources of REEs in these feedstocks in excess of 300 mg/kg. To achieve optimal extraction techniques and deploy commercially successful separation technologies, REE reserves must be identified. A complete characterization of the feedstocks is therefore important to understand physical characteristics such as porosity and grain size as well as geochemical characteristics such as mineralogy and REE-associations; all of which helps guide and formulate an effective extraction scheme. Using multimodal techniques, REEs have been identified in ion-exchangeable/colloidal phases and mineral phases in clay-rich samples underlying coal seams in the Appalachian Basin. X-ray diffraction (XRD) was performed to identify and quantify bulk mineralogy and clay composition. Scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) was used to identify REE bearing minerals. Focused ion beam – scanning electron microscopy (FIB-SEM) and advanced microanalysis with PerGeos software were used to reconstruct 3D volume renderings to estimate porosity and mineral distributions. REE-associated minerals identified through SEM-EDS included monazite and xenotime, which in most cases, averaged <2.5% of the bulk sample volume. Porosities in the clay matrices were typically below 6%. Synchrotron techniques using micro-X-ray Fluorescence mapping (µXRF) and micro-X-ray Absorption Near Edge Structure (µXANES) collected at Stanford Synchrotron Radiation Lightsource (SSRL) were employed to characterize distribution differences between light REEs (co-localized with Ca, P and Al in micrometer scale, and with Sr and Ba in millimeter scale) and heavy REEs (co-localized with Fe, S, and P) and to identify Ce species present in different clay-rich samples. Through these techniques, cerium was observed occurring in very fine-grained hotspots in the clay matrix and as carbonate or phosphate phases.

18.3 Characterization and Recovery of Rare Earth Elements from Powder River Basin Coal Ash

Mengling Stuckman, Christina Lopano, National Energy Technology Laboratory; Benjamin Hedin, Oak Ridge Institute of Science and Education; Bret Howard, Evan Granite, U.S. Department of Energy, National Energy Technology Laboratory; USA.

The reclamation of rare earth elements (REEs) from coal ash is proposed as an effective reuse of coal combustion wastes for commercial purposes and as an alternative way of REE mining. This study characterizes REE binding environments of Ca-Mg rich fly ash, bottom ash, and ponded ash derived from Powder River Basin (PRB) Coal. Distinguishing the chemical REE binding differences in the different ash fractions may aid in the development of a more cost-effective and environmentally friendly REE extraction; as compared to the published REE extraction from Al-rich Appalachian coal (APP) ash [1]. Results will inform optimized chemical extractions based on the geochemical characteristics to demonstrate significant potential of REE production from PRB ash samples.

Three ash samples (fly ash, bottom ash and ponded ash) derived from the combustion of PRB coal from one power plant in the state of Missouri were provided by Electric Power Research Institute (EPRI). Samples went through elemental analysis via $LiBO_2$ digestion and ICP-MS analysis, mineralogical analysis via XRD and SEM-EDS, sequential extraction to quantify REE distribution in different solid fractions and synchrotron-based microprobe analysis at Stanford Synchrotron Radiation Lightsource (SSRL), including micro-X-ray fluorescence for elemental distribution maps and micro-X-ray absorption near-edge spectroscopy for Ce speciation on REE hotspots. Preliminary results found that PRB while predominantly amorphous, generally consists of Ca,Mg-rich mineral phases (e.g., lime, periclase, anhydrite, merwinite, calcite and brownmillerite), in contrast to the aluminosilicate phases (e.g. mullite) commonly found in APP ash. Sequential extraction results showed 39%-46% REEs in PRB ash samples were extractable under pH 5, indicating significant REE association with Ca-rich mineral phases that are acid soluble. Synchrotron microprobe analysis further demonstrate frequent co-localization of light REE hotspots (10-100 µm) with Ca, as opposed to major REE co-localization within aluminosilicate phases in APP ash [2]. Significant Ce oxidation was observed in bottom ash sample with 10% Ce(IV) and pond ash sample with 30% Ce(IV), indicating more reactive REE deposition environments susceptible to oxidation along the PRB coal combustion chain. Synchrotron results also showed co-localization of heavy REEs with Fe phases in PRB ash samples. Overall characterization work has shown more mobile REEs in PRB ash compared to APP ash, due to different REE physical and chemical binding environments (e.g. Ca/Mg phases as opposed to Al/Si-rich glass phases) during coal combustion.

Based on thorough geochemical analysis, batch tests to optimize REE leaching from PRB fly ash were conducted using various acids (e.g., nitric, hydrochloric, citric and acetic aids, etc.) and concentrations. The preliminary results demonstrate 100% REE extractability from PRB ash using dilute acids at room temperature in short period of time. Heavy REEs and light REEs can be leached from the fly ash separately using different acid conditions sequentially extracting Ca phases and Fe phases.

Ref: [1] Lin, R., M.Y. Stuckman, et al., Fuel, 2018. 232: p. 124-133.2. [2] Stuckman, M.Y., C.L. Lopano, and E.J. Granite. International Journal of Coal Geology, 2018. 195: p. 125-138.

18.4 Characterization of Rare Earth Elements in Coal Mine Drainage Treatment Solids

Benjamin Hedin, Oak Ridge Institute of Science and Education, Mengling Stuckman, Christina Lopano, National Energy Technology Laboratory; Rosemary Capo, University of Pittsburgh; USA.

Polluted coal mine drainage (CMD) from the eastern U.S. coalfield contains elevated concentrations of acidity and dissolved Fe, Al, and Mn and is also enriched in rare earth elements (REE) by up to three orders of magnitude over unpolluted groundwater (1, 2). Over 500 metric tons per year of REE can be recovered from Appalachian CMD alone (3). Mine drainage treatment systems, designed to precipitate dissolved metals, can sequester >90% of dissolved REE into these precipitates (treatment solids). These solids, landfilled at cost to treatment system operators, can be a promising REE mining source. Our study aims to: (1) determine REE sequestration in different treatment technologies (e.g. active vs. passive systems) and (2) determine micro-scale REE geochemical associations in treatment solids from different treatment systems. This information can be used to guide REE recovery efforts from existing treatment systems, inform the design of new treatment systems engineered to concentrate REE into treatment solids, and optimize REE extraction from treatment solids.

To understand the REE variation and geochemical relationships in treatment solids, a database of >250 treatment solid samples from across Appalachia was constructed and analyzed. Specific treatment systems were characterized by collecting water and treatment solid samples. Water samples into and out of treatment cells and treatment solids underwent elemental analysis by ICP-MS. Selected powdered treatment solids underwent XRD for mineralogical analysis and 7-step sequential extractions to quantify REE distribution in different solid fractions. Thin sections of selected solids were analyzed via SEM-EDS, synchrotron micro-X-ray-fluorescence (µ-XRF), and synchrotron micro-X-ray absorption near-edge spectroscopy (XANES) at SSRL.

REE concentrations in CMD treatment solids range from <12 ppm to almost 2,000 ppm and are positively correlated with the sum of Al and Mn contents in the solids (R2 = 0.76) (4). REE removal from the CMD water during the treatment process is pH dependent, with limited REE removal at pH < 5 and substantial REE removal at pH > 5 (5, 6). REE are most likely to be enriched in treatment solids precipitated during the transition from low pH to circumneutral pH. Sequential extractions on treatment solids showed that limited REE are associated with the exchangeable fraction in treatment solids (< 10%) and > 80% of REE are associated with acid soluble mineral phases. On the micro-scale, µ-XRF elemental mapping showed that REE co-localized with Mn as co-precipitates on the surface of the treatment solids from a limestone based passive treatment system (5). Preliminary data suggests that light and heavy REE can be associated with different mineral phases in complex treatment solids (e.g. those with Al, Fe, and Mn phases).

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18.5 Quantitative Rare Earth Elemental Analysis by Laser-Induced Breakdown Spectroscopy

Samuel M. Clegg, Ann Ollila, Adriana Reyes-Newell, Zhenghua Li, Los Alamos National Laboratory, USA.

Laser-Induced Breakdown Spectroscopy (LIBS) has been used to qualitatively analyze the presence of Rare Earth Elements (REE) within a coal matrix. LIBS involves focusing a Nd:YAG laser (1064 nm) onto the surface of the sample. The laser ablates material from the surface to generate an expanding plasma containing electronically excited atoms, ions, and small molecules. These electronically excited species emit light at diagnostic wavelengths as they relax to lower states. The LIBS analyses were completed with the ChemCam laboratory instrument at Los Alamos National Laboratory. The ChemCam laboratory instrument is a replica of the ChemCam instrument currently operating on the NASA Curiosity rover. We prepared 28 calibration samples consisting of up to five REEs at various concentrations in a coal matrix. Each of these 28 samples were probed in three locations with 30 laser shots. The average spectra from each of these three locations and the REE compositions were input into a Partial Least Squares (PLS) multivariate model. A full cross-validation analysis was completed where each calibration target was removed from the analysis and treated as an unknown from which the accuracy was determined. In this paper, the LIBS experimental setup and data analysis will be discussed.

SESSION 19
CARBON MANAGEMENT II
Steve Carpenter and Nick Siefert

19.1 Status of Technology Development at the National Carbon Capture Center

Doug McCarty, Southern Company, USA.

Sponsored by the U.S. Department of Energy (DOE), the National Carbon Capture Center (NCCC) is a cornerstone of U.S. innovation in advancing fossil energy technology solutions. Bridging the gap between laboratory research and large-scale demonstrations, the NCCC evaluates carbon capture processes from third party developers, focusing on the early-stage development of the most promising, cost-effective technologies for future commercial deployment. Since its creation in 2009, the center has achieved more than 100,000 hours of technology testing, with research through mid-2017 focused on post-combustion carbon dioxide (CO_2) capture, gasification, and pre-combustion CO_2 capture technologies. After completing more than 25 projects in the gasification and pre-combustion carbon capture areas, the NCCC concluded this work in response to changes in the project scope to focus more on postcombustion capture for natural gas and coal power generation. As the demand for post-combustion CO_2 capture options grows, work in this area continues to bring new technologies closer to the marketplace. The post-combustion carbon capture facilities include solvent test units to evaluate developers' solvents at benchor pilot-scale, as well as sites for developers' bench- or pilot-scale test skids. Testing utilizes flue gas from Alabama Power's Plant Gaston Unit 5, an 880-megawatt base-loaded, coal-fired boiler. Evaluation of developing technologies using actual flue gas under industrial conditions provides critical information on material and process suitability for scale-up to commercial applications. While several test campaigns have been conducted under simulated natural gas conditions (with air dilution), the NCCC is currently making plans for significant infrastructure additions to support carbon capture testing under actual natural gas-fired conditions. Work is also planned for evaluations of CO_2 utilization technologies. More than 30 post-combustion projects have been completed, including three solvent projects that progressed to commercial demonstration. While the advanced solvents and solvent processes offer economic advantages over the standard baseline solvent (monoethanol amine, or MEA), the NCCC also promotes the development of innovative carbon capture processes that could offer more significant cost reductions, such as membranes, enzymes, and sorbents. Several of these processes have progressed with scale-ups to larger-scale testing or commercial demonstration. Because reduction of CO_2 emissions is an international issue, the NCCC has been active in establishing test collaborations with international groups, supporting technology developers from seven countries to date. The NCCC also assumed leadership and was the host site of the Carbon Capture International Test Center Network (ITCN) for the past two years. Formed in 2012 in collaboration with DOE's Office of Fossil Energy, the ITCN facilitates knowledge-sharing among carbon capture test facilities around the world to accelerate the commercial deployment of carbon capture technologies. While chairmanship of the ITCN was transferred to the United Kingdom Carbon Capture and Storage Research Centre during 2018, the NCCC continues to actively participate in the network's leadership and technology transfer mission.

19.2 CCUS (CO_2-EOR), ISO 27916, & 45Q: Wyoming's Triple Threat – the Cowboy Unicorn

Steven M. Carpenter, University of Wyoming, USA.

Wyoming is special in that has a natural resource aware and likely a CCUS-willing citizenry, a positive and flexible regulatory framework for CCUS, a supportive legislature and executive branch, and most importantly, it has the site characteristics needed to do both CO2-EOR and saline storage. The Wyoming Integrated Test Center (ITC) located at Basin Electric's Dry Fork Station is studying options to turn CO2 it into commercial, beneficial re-use materials – this provides a CCUS project with a third option. This makes the ITC/Dry Fork Station the only facility on the planet that has the capacity, when completed, to deal with all three options for CO2 – 1) beneficial re-use, 2) CO2-EOR, and 3) saline storage.

With the passage of 45Q there is great discussion over the "financibility" of commercial scale CCUS. While 45Q does not eliminate all the financial risks it does provide an option to allow CO2-EOR to provide a permitting and storage "back stop" to saline only CCUS projects. Many have been wrestling with how to address the EPA/DOE/IRS lack of guidance as to the definition of "safe and secure storage". The current guidelines only allow for the use of EPA GHGRT Subpart RR reporting. Many in the industry have technical, policy, and corporate issues with EPA GHGRT Subpart RR. The International Standards Organization's (ISO) Technical Committee 265 entitled Carbon dioxide capture, transportation, and geological storage's scope is to standardize the design, construction, operation, environmental planning and management, risk management, quantification, monitoring and verification, and related activities in the field of carbon dioxide capture, transportation, and geological storage (CCS). This effort includes CO_2-EOR or CCUS and the newly published CO2-EOR ISO Standard 27916 may be an acceptable alternative to EPA's Subpart RR. The possibility of an EPA Subpart RR AND an EPA Subpart UU + ISO 27916 may just move the needle enough to spark the commercial deployment of CCUS that has been sought after for some time.

Imagine a place that could offer multiple coal fired power plants that could beneficially reuse CO2 from the flue gas, AND; supply CO2 for CO_2-EOR flooding, AND; store CO2 in saline storage or "stacked storage" sites, AND facilitate 45Q tax credits to support the project financing. No, this is not a unicorn, but rather Wyoming's triple threat. One, if not the only place on the planet that has the capacity to deal with all three types of CO2 from a commercial CCUS project, afford options for "safe and secure storage" via Subpart RR OR UU + ISO 27916, and consider options to ensure that there are multiple locations within Wyoming where this is possible.

This presentation will discuss the transdisciplinary approach that has resulted in Wyoming providing this world-class opportunity to advance commercial scale CCUS, current and prospective sites, potential business structures, potential realization of carbon negative oil, and the application of newly drafted International Standards for both CO2 Storage and CO2-EOR.

19.3 A Comparison of CO_2 Storage Quantification Methodologies

George Koperna, Advanced Resources International, Inc.; Michael Godec, Advanced Resources International, Inc.; Steven M. Carpenter, University of Wyoming, USA.

With the recent expansion of the U.S. Internal Revenue Code (IRC) Section 45Q tax credit for CO2 storage, numerous projects are seeking to garner this incentive for their respective projects. Guidance from the Internal Revenue Service (IRS) recommends that the Environmental Protection Association (EPA) CO2 reporting rules, particularly Subpart RR of the Greenhouse Gas Reporting Program (GHGRP), be used to quantify CO2 incidentally stored during CO2-EOR, as well as for the injection of CO2 for storage in depleted hydrocarbon and saline reservoirs. However, there now exists two additional means of established incidental and pure storage quantification mechanisms that may serve as proxies for the GHGRP requirements.

More than five years ago, the International Organization for Standardization (ISO) formed technical committee 265 (TC-265) dealing with carbon dioxide capture, transport and geological storage. TC-265 was subdivided into six working groups, and international standards have been generated for post-combustion capture, pipeline transportation, geological storage (without storage quantification), and CO2-EOR (with incidental storage quantification). An international standard for depleted hydrocarbon reservoir and saline storage quantification is in development and, when combined with the CO2-EOR standard, provides for all instances of CO2 storage quantification.

Similarly, the Society of Petroleum Engineers is working to develop a storage resources management system (SRMS). Based on their petroleum resources management system (PRMS), which is the industry standard oil and gas reserves accounting system, the SRMS for depleted hydrocarbon and saline storage was published in 2018. Currently, the SRMS committee is working to publish a guidelines document and then will look to add CO2 incidentally sorted during EOR to the system.

This paper/presentation will look to compare the methodologies for each of the three quantification mechanisms. The paper will describe what each methodology is intended to address (and what it is not), compares and contrasts the methodologies and, where appropriate, the results from their application, and highlights the supporting materials necessary to quantify and validate CO2 storage.

19.4 Regional Economic Impacts of Carbon Capture and Sequestration

Joshua J. Stanislowski, University of North Dakota Steven M. Schlasner, Bruce C. Folkedahl, Michael L. Swanson, and Melanie D. Jensen,
University of North Dakota, USA.

Regional economic impacts are a critical piece of the decision process surrounding carbon capture, utilization, and sequestration (CCUS) implementation. Integration of carbon capture technologies with the existing coal fleet not only helps to ensure the longevity of an existing industry, but significant number of jobs are created at the capture plant during the construction and operational periods, which results in additional job creation through indirect and induced effects. Local suppliers will see an uptick in sales due to the high demand for construction materials, which is considered an indirect impact on the local economy. Workers spend money on housing, food, and entertainment that can induce additional job creation. The ripple effects of a project such as this can last for many years and result in increased tax revenue to the state and other localities. Permanent jobs are created during the operational phase at both the plant and oil wells that are ready for enhanced oil recovery (EOR) operations. The incremental oil production can also increase tax revenues to the state. This presentation will review the potential regional economic impact of wide-scale CCUS technology implementation on coal-fired power plants and in oil fields in North Dakota.

The economic impacts of activity in the energy sector can be determined through the use of input–output (I-O) models. There are many commercially available I-O software models; the three most commonly used are the Regional Input–Output Modeling System (RIMS-II), Impact Analysis for Planning (IMPLAN), and Regional Economic Models, Inc. (REMI). All of the I-O analysis models produce the economic impacts of three basic effects-direct, indirect, and induced, which, when totaled, are equivalent to the total economic impact/change based on the circumstance modeled. The direct effect is essentially the amount of spending as a direct result of the change in the industry sector under study. For the purposes of this study, this would be the amount of capital expenditure for the construction of a CO2 capture system at a power plant and the construction of the pipeline required to transport the CO2 to the oil fields for EOR activity. This direct effect would include not only the capital plant expenditures, but the salaries paid to the employees by the companies building the plant. The indirect effect would be the amount of economic impact on the state from the contractors and subcontractors purchasing goods from local/state entities such as steel, concrete, welding supplies, etc. The induced effect is the change in economic impacts due to employee spending of earned income for restaurants, clothing, cars, visits to doctors, etc.

The EERC has evaluated the economic impact of CCUS technology implementation in the state of North Dakota. The estimated capital and operational costs for these activities have been determined and then analyzed using the IMPLAN model with region specific modifications. The direct, indirect, and induced effects have been determined for a number of scenarios. This presentation will review the results of these studies and show the positive regional economic impact that can be realized when CCUS technologies are deployed.

19.5 A Forward-Looking Assessment of Advanced Membrane Technology for Cost-Effective Post-Combustion Carbon Capture

Haibo Zhai, Carnegie Mellon University, USA.

This study offers an integrated vision for advanced membrane technology for cost-effective post-combustion carbon capture with respect to advanced materials, process engineering, engineering economics, and technology learning. To inform development of new generation polymeric membranes, a plant-level techno-economic analysis is performed to explore major membrane property targets required for cost-effective CO2 capture. To be competitive with amine-based nth-of-a-kind (NOAK) technology or meet a more ambitious capture cost target (e.g., $30/tonne) for 90% CO_2 capture, advanced membranes should have a higher CO2 permeance than 2,250 GPU and a higher CO2/N2 selectivity than 30 if their installed module prices are higher than $\$50/m^2$. To assess learning experience required for advanced technology using such high-performance membranes toward commercialization, a hybrid approach that combines top-down learning curves with the bottom-up techno-economic analysis is applied to project the cumulative installed capacity necessary for the evolution from first-of-a-kind to NOAK systems. The estimated learning scale for advanced membrane technology is more than 10 GW, depending on multiple factors (e.g. membrane properties, initial capital cost, learning rates, and cost target). Implications for research, development, and policy are discussed.

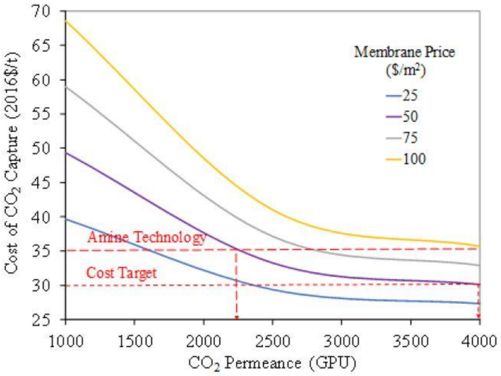

Fig. 1. Variability in Cost of CO_2 Capture by Membrane Permeance and Price of NOAK Membrane Technology

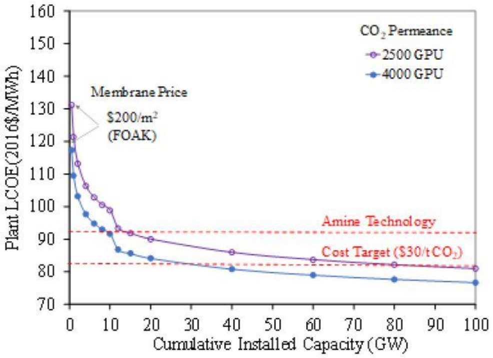

Fig.2. Evolution of Plant Levelized Cost of Electricity with Cumulative Installed Capacity of Membrane-based Capture Systems: Initial Membrane Cost: $200/m2, Learning Rates: 11% in Capital and 22% in O&M

SESSION 20
COAL BED METHANE AND SHALE GAS
Dan Connell and Richard Winschel

20.1 Global Coal Mine Methane and Coalbed Methane Developments

Clark Talkington, Advanced Resources International, Inc.; Valerie Askinazi, U.S. EPA Coalbed Methane Outreach Program; Kyeong Pil Kong, Advanced Resources International, Inc.; USA.

Methane is a greenhouse gas (GHG) produced during the mining of coal. Mitigation of coal mine methane (CMM) emissions has become an important global policy priority driven by methane's relatively short atmospheric life and its capacity to be productively used in many applications. Coal production ranks fourth among the major sources of anthropogenic CH4 emissions, accounting for 9% of global emissions, but the industry could realize significant emission reductions by employing projects integrating available technologies to reduce methane emissions, especially at very large, gassy underground mines. The United States Environmental Protection Agency (U.S. EPA) estimates that current global coal mine methane (CMM) emissions total around 640 million metric tonnes of CO_2 equivalent (MMTCO2e) using the GWP of 21 in the IPCC Second Assessment Report.1 This equates to 45 billion cubic meters of pure methane. At a GWP of 25 used in the Fourth Assessment Report, methane emissions total 761 MMTCO2e.
The Global Methane Initiative (GMI) is an international public-private partnership focused on reducing barriers to recovery and use of methane as a clean energy source. The GMI, through collaboration with other international organizations, the private sector and other stakeholders promotes best practices to capture and use CMM to mitigate methane emissions. While CMM project development cannot address all GHG impacts

from coal production and use, it can provide an interim solution to significantly reduce the footprint of the coal industry. Currently, the GMI has documented over 200 operating CMM projects across the globe, demonstrating the technical and economic viability of the various CMM technologies and practices.

This presentation will: (i) introduce the GMI and discuss GMI's support for CMM emissions reductions and international CMM project development; (ii) review global CMM emissions; (iii) review ongoing activities in countries accounting for most CMM emissions, notably Australia, China, India, Russia, Poland, Ukraine, and the United States; (iv) provide updates on other countries where the CMM and CBM industries are in the early stages of development; and (v) present a brief case study of GMI support to improve methane management at an underground coal mine in China.

20.2 Impacts of Solution Composition and Temperature on Ra-226 Removal by Barite (Baso4): Comparison of Experimental and Modeling Results

Alen Gusa, University of Pittsburgh; Hamid Al-Khashab, Joseph R. V. Flora, University of South Carolina; Radisav D. Vidic, University of Pittsburgh; USA.

Expansion of the unconventional gas industry with development of hydraulic fracturing and horizontal well drilling led to increasing environmental concerns regarding the effect of this industry on freshwater resources. Flowback and produced water generated during the exploitation of a well has very high concentration of total dissolved solids (TDS up to 345 g/L) that are mainly comprised of alkali and alkaline earth metals. Naturally occurring radioactive material (NORM) is present in this water in concentrations up to four orders of magnitude higher than the EPA standards for drinking water (i.e., 5 pCi/L) and industrial effluents (i.e., 60 pCi/L). Major component of NORM in this water is Ra-226 isotope which is also a serious environmental threat due to its long half-life (i.e., 1,600 years). Various treatment approaches were investigated to enhance the removal of Ra-226 from industrial effluents, including co-precipitation, post precipitation reactions, ion exchange resins, etc. One of the most effective ways for Ra-226 sequestration is through co-precipitation with barium sulfate (Barite) that has been well-studied. However, the mechanism of Ra-226 removal by preformed barite is yet to be fully unraveled.

This study focuses on understanding the mechanisms of Ra-226 removal by barite as a function of solution composition and temperature of the solution. Ionic strength of up to 1 M was used to investigate the impacts of salinity on the efficiency of Ra-226 uptake by barite particles. The impact of different monovalent and divalent cations (i.e., Na^+ , K^+ , Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) on Ra-226 adsorption on barite were analyzed to understand the impact of ionic radius and diffusivity of competing species in the solution. One of the major findings of this study is that the removal of Ra-226 in the presence of different ions can be correlated to variations in zeta potential of barite when exposed to these ions. Ra-228 uptake at different temperatures (i.e., 0-3, 21 and 40 °C) was evaluated to determine the main mechanism of Ra-226 uptake by barite and elucidate the differences between adsorption and surface dissolution/recrystallization phenomena. Experimental results are compared to molecular dynamics modeling and used to further expand our understanding of Ra226 removal, which will be discussed at the conference.

20.3 Casing Stability for Gas Wells in Longwall Abutment Pillars of Active Mines and a Characterization of Migration Potential for a Hypothetical Well Breach

Schatzel, V Gangrade, E Watkins, C Hollerich, J Addis, W Su, NIOSH/PMRD, USA.

More than 1500 unconventional shale gas wells have been drilled ahead of longwall mining in PA, WV, and OH. These gas wells are designed to be protected by chain pillars or abutment pillars such that the well casing experiences minimal movement in response to longwall mining activity. Longwall mining induces surface and subsurface subsidence and stress changes in the overburden. The placement of gas wells has been guided by the 1957 PA Gas Well Pillar Regulations used nationwide as the best well placement input available. However, since that time longwall mining has become common in the US and overburden depths have greatly increased making the 1957 PA Gas Well Pillar Regulations no longer applicable. Ground movement within these longwall pillars is being characterized experimentally by NIOSH researchers, and finite element modeling is being conducted and calibrated on the basis of the field data to extrapolate results to other well sites.

Differences in overburden depth, geology, topography and mining methods can create a range of ground responses in subsidence and induced fracture networks near gas wells in abutment pillars. These parameters can strongly effect well casing stability. There are examples of gas well hazards having occurred in this region. A recent 2019 failure of a shale casing occurred in southwestern Pennsylvania during completion operations where high pressure production gas reached nearby shallow gas wells and vigorously vented to the surface producing a hazardous environment. Leakage from gas wells in close proximity to longwall excavations resulted in many ignitions at the longwall face at a Pennsylvania longwall mine. Stray gas in surface dwellings and water wells have been documented in Ohio, Pennsylvania, and West Virginia.

NIOSH research is focused on worker health and safety and is conducting research to assist industry, regulatory, and permitting personnel in developing new guidelines related to safe distances for gas wells to be placed near active longwall mining. Gas wells will be plugged during mine-by where typical Marcellus shale wells are expected to experience pressures of about 3000 psi. From a ventilation research perspective, NIOSH researchers were asked to characterize a worst case scenario where a temporarily shut-in shale well experienced a breach proximal to active mining. The transport of this gas towards the mine void and the safety hazards it might produce is a key task for this NIOSH research effort.

20.4 Porosity and Fractal Dimensions of Lower Permian Barren Measures Organic-Shales, Damodar Valley, India,

Bodhisatwa Hazra, Co-Authors: Ashok K. Singh, Pradeep K. Singh, CSIR-CIMFR;
Pudi Srinivasa Rao, Koushik Mahanta, Tata Steel Limited; INDIA.

Twelve shale samples belonging to the Lower Permian Barren Measures Formation collected from a borehole from Jharia basin, India were characterized in terms of their hydrocarbon-generation potential and porous structures, using the techniques of Rock-Eval and low-pressure N2 gas adsorption. The TOC content of the studied shales was observed to vary between 2.08-6.15 wt %. The Tmax values (temperature-peak of S2 pyrolysis curve) were observed to vary between 445-460 °C, indicating them to be placed in the peak to late mature stage of thermal maturity. Kerogen at this stage of thermal maturity is capable of generating hydrocarbons (oil or condensate). The free hydrocarbon-compounds released during the initial isothermal stage (S1 curve), was observed to vary between 0.11 to 0.89 mg HC/g rock. Interestingly, the shale samples marked by highest thermal maturities showed the least S1, while the sample marked by least thermal maturity showed highest S1 (Sh7). The sample Sh7 was also marked by highest TOC content and S2, in addition to S1. Although not distinctive, a negative trend was observed in the HI-Tmax cross-plot for the samples, with the sample marked by highest Tmax showed least HI. The results thus indicate that with increasing thermal maturity, hydrocarbons are expelled from the horizon. In general, HI values varying between 66-206 mg HC/g TOC, indicate input of dominantly type III organic-matter.

The BET SSA of the shales was observed to vary between 7.04 to 23.77 m2/g rock. Although previous works by several researchers have documented that SSA in shales is primarily controlled by their TOC content, for the studied suite of samples no relationship was observed between the above-mentioned two variables. On the other hand, although not distinctive, the influence of Tmax was on BET SSA was observed to be more pronounced. The sample marked by highest Tmax, was also marked by highest SSA. The average pore radius of the samples, ranging between 19.52 to 30.74 Å, was observed to be strongly (negatively) correlated with the thermal maturity levels of the organic-matter (R2= 0.75). The lower relative pressure (P/P0< 0.50) fractal dimension D1 (where adsorption is dominantly controlled by van der Waals forces) and the higher relative pressure (P/P0= 0.50-1) fractal metric D2 (adsorption dominantly controlled by capillary condensation), were both observed to be highest for the shales marked by highest thermal maturity levels, further establishing the influence of thermal maturity on pore structural attributes. The D1 and D2 were observed to vary between 2.55-2.62 and 2.68-2.81, respectively, indicating presence of complex pore surfaces within the shales. The higher pore volumes, presence of complex microporous structures, considerable organic-richness, higher thermal maturities, makes the Barren Measures shales from Jharia basin excellent targets for CO2 sequestration.

SESSION 21
COAL ASH MANAGEMENT III
Tarunjit Butalia

21.1 Designing the Ash Beneficial Use Center

Benjamin Gallagher, Ken Ladwig, EPRI, USA.

The Ash Beneficial Use Center (ABUC) is a research facility being constructed at Plant Bowen, a coal-fired power plant in Cartersville, Georgia, USA. ABUC is focused on new technologies that enable the use of coal combustion products (CCPs), especially CCPs harvested from existing impoundments and landfills. ABUC was formed in response to the challenge for sustainable management of over 2 billion tons of CCPs currently stored in impoundments and landfill in the US. EPRI identified a gap in capabilities, where ideas for beneficial use were tested at small "benchtop" scale but did not have a simple path to orders of magnitude to full scale operations. The major goals of ABUC are to evaluate technologies for beneficial use, including conformance of the end products with real world specifications, and to accelerate commercialization of promising beneficial use technologies.

ABUC consists of three major areas, CCP preparation, technology testing, and product verification. This paper will focus on the design of the CCP preparation area. The product verification lab will also be discussed.

The US Federal Rule requires CCP unit closure activities be completed on a limited schedule, and closure projects may need to move in excess of 1,000 tons per day for compliance. A throughput of 1,000 tons per day is also similar to ash handling at large coal-fired powerplant. To allow for one demonstration at 1/10 of full-scale, ABUC's infrastructure is designed for operation at maximum throughput of 100 tons per day. Recognizing the that most new beneficial use technologies have only been tested at benchtop scale, ABUC infrastructure is configured with storage to allow limited operation of large infrastructure, once every week or two, and still accommodate several smaller pilot tests operating at a size of 1 to 10 tons per day.

CCPs harvested from impoundments and landfills are quite varied in characteristics, however they are all generally wetter than useful and contain certain amount of undesirable materials (non-CCP debris and off-size CCP). ABUC's processing infrastructure is aimed at transforming harvested CCPs into a ready to use ingredient by reducing moisture content and adjusting particle size distribution. The feed system includes an unloading bay to receive covered dump truck shipments of CCPs, and a feeder to the debris removal. Debris removal includes a scalping screen to remove harmful oversize non-CCP materials, and an optional second screen to separate large bottom ash particulates. The scalped feed leaves debris removal by conveyor to the flash drying apparatus, where moisture is reduced to less than 1%. Dried CCPs are pneumatically conveyed to the primary storage. Pneumatic unloading of bulk tankers of freshly produced CCPs directly to primary storage is also provided. Full-size air classification is provided to separate coarse and fine fractions of dried CCPs. Smaller scale processes for grinding and dry blending are also provided.

The lab serves two functions: quality control for processed CCPs feed to the test bays, and verification of finished products. The onsite portion of the lab includes laser diffraction analysis for determining particle size distribution and ovens for determining moisture and carbon content. In addition, a gas pycnometer, surface area analyzer, and X-ray florescence analyzer are available to better characterize the CCPs. On-site product verification testing includes compressive strength testing.

21.2 Characterization of CCP Impoundments to Determine Suitability for Beneficial Use

Robb Erwin, Ross Gorman, The SEFA Group, USA.

The continuing decline of coal utilization for energy production has resulted in a limited and declining supply of CCPs for beneficial use applications. In order to meet growing market demand and mitigate environmental risk, harvesting of impounded CCPs for beneficial use is becoming an increasingly desired solution. In order to fully evaluate the risks, beneficiation opportunities, and economic value of CCP ponds and landfills, the impoundments must be strategically characterized before harvesting.

In this presentation, the methods by which a CCP impoundment can be characterized will be reviewed. In general, one of the first steps is engineering a sample plan informed by pond or landfill profile and any known historical data related to the development of the site. Test methods are then selected for the samples in order to evaluate material characteristics that impact specific beneficial use opportunities. Impoundment profiles are then generated to give a comprehensive understanding of the in-situ CCP material.

21.3 Reclaiming and Recycling Coal Ash for Beneficial Use

Bill Fedorka, Robert Erwin, SEFA, USA.

Not long-ago coal-fired power plants produced more than half of the electricity in the United States. That share was cut to just 30% in 2017 after an unprecedented rate of plant retirements. Some industry estimates project that number to be cut in half by 2040.

Due to the acceleration of closures, as well as increased environmental pressures, more and more utilities will be facing crucial decisions related to closure plans of legacy coal ash impoundments.

One possible solution that should be considered in most applications is "Encapsulated Beneficial Use". This approach is consistent with what the industry has been doing for years: using ash as a performance-enhancing additive in concrete and other composites. Consequently, utilities have an even greater incentive to see that coal ash goes to beneficial uses such as concrete– namely, reducing their disposal costs in cases where clean closure may be required as well as improving environmental stewardship.

The SEFA Group, a longtime leader in the fly ash utilization industry, with nearly two decades of thermal beneficiation experience, has commercialized the ability to process coal ash reclaimed from existing storage ponds or fills without the need of additional energy inputs to their Staged Turbulent Air Reactor (STAR) technology. The latest generation facility came online early 2015 at Santee Cooper's Winyah Generating Station, and three more are under construction in North Carolina.

The STAR product is a highly desirable additive to ready mix concrete. The STAR ash replaces a portion of Portland cement resulting in not only decreased cost per yard, but improved strength and durability.

In many applications, beneficiating coal ash and recycling in concrete results in significant savings when compared to disposal in landfills. Beneficial use also eliminates the long-term environmental liability of leaving ash in the ground. In addition, the use of fly ash as a replacement for Portland cement results in a global reduction in CO2 emissions.

This paper will discuss various aspects of the technology, operating experience, and review the economic justification for beneficiation versus disposal in lined landfills.

21.4 Coal Ash in the Chesapeake Bay Watershed

Paul Petzrick, Maryland Department of Natural Resources, USA.

The Chesapeake Bay is a treasured aquatic resource of the Mid-Atlantic Region. The good fortune of the major rivers feeding the Bay and the Bay itself providing cooling water for electric power plants in close proximity to the large Appalachian Coal Basin provided for cheap production of electricity for over a century. This fortunate combination is now leaving behind millions of tons of coal ash to contaminate the waters of the Region so important to its growing population. If not addressed this contamination will persist for centuries through the slow leaching of coal ash.

This presentation will identify known coal ash deposits in the Region and cite examples of those being recovered for beneficial use and marketed on an ever-broader scale. In so doing it is intended to attract other vendors to investigate sharing in this unique business opportunity. Over 100 coal ash deposits have been identified in the five States that share the Chesapeake Bay Watershed. In Maryland there are coal ash storage sites created in response to the Maryland Pozzolan Act of 1974 which required that coal ash be used immediately or stored for future use. These deposits may be especially attractive business opportunities having known quantities and properties.

21.5 Fly Ash Beneficiation Using Triboelectric Separation

Cesar A. Constantino, Separation Technologies LLC, a Titan America Business, USA; Lewis Baker, ST Equipment & Technology LLC, UK; Abhishek Gupta, Frank Hrach, ST Equipment & Technology LLC, USA.

Tribo-electrostatic separation has been used for the commercial beneficiation of coal combustion fly ash to produce a low carbon product for use as a cement replacement in concrete for over twenty years. With 24 separators installed in 17 locations across the world, ST Equipment & Technology LLC's (STET) patented electrostatic separator has been used to produce over 17.5 Million tons of low carbon product that has been recycled for use in concrete or cement production.

Commercial tribo-electrostatic beneficiation of fly ash has been performed primarily on dry "fresh" ash. Reductions in the quantity of dry fly ash generation and requirements to empty historical ash landfills and ponds has created the need to develop a process to reclaim and beneficiate landfilled or ponded ash.

The authors have determined the effect of moisture exposure on separation efficiency of multiple ash samples that have been reclaimed from landfills and ponds at the pilot-scale. Test results have demonstrated that concrete performance for the low carbon fly ash product produced using tribo-electrostatic separation is equivalent for reclaimed fly ash and "fresh" fly ash produced from the same source.

A technical and economic evaluation of tribo-electrostatic separation and combustion-based processes for beneficiation of reclaimed fly ash was performed. This study confirmed that the tribo-electric process is significantly lower total cost of operation and generates significantly lower air emissions than combustion-based processes for beneficiation of reclaimed fly ash.

SESSION 22
PYROLYSIS II
Francis Lau, Alexander Sobolewski

22.1 An Approach for Quantifying Transferable Hydrogen in Pyrolyzing Coals

Koyo Norinaga, Professor, Nagoya University, Tetsuya Fukuoka, Hiroshi Machida, Wei Zhang, Nagoya University, JAPAN.

The authors proposed an approach to quantify transferable hydrogen of coal upon heating. Coal pyrolysis involves condensation reactions of aromatic ring systems that induce hydrogen formation and aromatic cluster growth. The 13C- and 1H-NMR data for the coal and the heat-treated char samples made the quantifications of the average size of aromatic clusters. The amount of hydrogen possibly generated by the aromatic growth was stoichiometrically estimated. The consideration on the fate of the hydrogen formed within the pyrolyzing coal suggested the possible conversion routes of hydrogen in solid/liquid phases, including the hydrogen used for hydro-deoxygenation and the hydrogen transferred for stabilizing radicals formed by thermal decomposition. The amount of hydrogen consumed for hydro-deoxygenation can be estimated from the difference between the amounts of pyrolytic water released into gas phase and water formed by hydroxyls condensation. With the balance, it was eventually possible to estimate the amount of the transferable hydrogen. According to the proposed approach, it can be revealed that the bituminous coal, showing plasticity, had 3.5 mol/kg-coal transferable hydrogen, whereas sub-bituminous coal, a non-caking coal, exhibited much less transferable hydrogen, 1.3 mol/kg-coal during pyrolysis up to 500 °C.

22.2 Syngas-Fired Allam Cycle Project Update

Joshua J. Stanislowski, Jason D. Laumb, University of North Dakota Energy & Environmental Research Center; Xijia Lu, Mike McGroddy 8 Rivers Capital, LLC; USA.

The Allam Cycle, a high-pressure, highly recuperative, oxygen-fired, supercritical CO2 cycle, makes carbon capture part of the core power generation process. The Allam Cycle utilizes supercritical CO2 as a high-pressure working fluid through a compact high-pressure turbine and will be demonstrated on natural gas at the 50-MWth scale. Interest exists to operate the Allam Cycle on syngas-based feedstocks. The Energy & Environmental Research Center and 8 Rivers Capital, along with industry partners in North Dakota and the U.S. Department of Energy, initiated a project to build a large pilot Allam Cycle system operating on syngas. This project builds on prior work performed by the team to overcome key technical challenges in converting the Allam Cycle to a syngas-fired system. Phase I of the project has been completed and consisted of site selection and cost estimating for the large pilot system. This presentation reviews the status of the syngas-fired technology and details plans for a large coal-fired pilot-scale Allam Cycle unit in North Dakota.

22.3 Steam Reforming of Toluene as a Tar Model Compound Over Ni/Biochar: The Effects of Inherent Potassium

Chen Xu, Zhen-yi Du, Hong-da Ma, Shi-qi Yang, Jie Feng, Wen-ying Li, Taiyuan University of Technology, CHINA.

Tar from biomass gasification process can be effectively removed by the catalytic steam reforming technology. In this paper, biochar supported nickel (Ni/BC) catalysts were prepared for steam reforming of toluene, a tar model compound derived from biomass. The effects of inherent alkali metals and alkaline earth metals in biomass char, especially potassium of high content on the activity and stability of Ni/BC catalysts were investigated. Firstly, three Ni/BC catalysts were prepared namely raw, water washed, acid washed samples. The potassium content of them was 2.50%, 0.42% and 0.01% respectively. Then steam reforming of toluene was studied under the conditions of 450, 500, 600 °C respectively. The feeding rate of water was adjusted to achieve a steam to carbon ratio of 3. The space time defined as the ratio between the mass of catalyst and the mass flow rate of toluene of 0.5 h. The results indicated that the presence of potassium effectively aided the activation of water and decreased the reaction temperature. The Ni/BC catalysts with high potassium content had high catalytic activity at low temperatures. Nevertheless, under the reaction temperature of 600 °C, the stability of Ni/BC catalysts with high potassium content was poorer than their counterparts, and the catalysts were completely deactivated in about 1.5 hours. It was attributed to the increased reaction severity between steam and the char support. Consequently, the activation of water by potassium in the char support was revealed, and this effect can be properly used to enhance the low temperature reforming capability of Ni/BC catalysts.

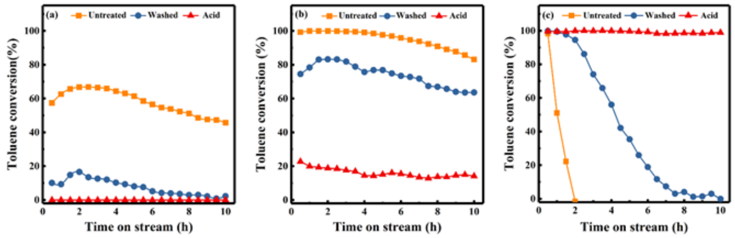

Figure: Toluene conversion of Ni/BC catalysts at different temperatures: (a) 450 °C (b) 500 °C (c) 600 °C

22.4 Spectral Characteristics of Diesel and Coal Water Slurry Flames in an Entrained-Flow Gasifier

Huiwen Zhu, JiaBao Yang, Yan Gong, QingHua Guo, YiFei Wang, GuangSuo Yu, East China University of Science and Technology, CHINA.

The spontaneous emission spectra of the flame are closely related to flame characteristics such as flame structure and temperature distribution. And the combustion state of the flame can be reflected clearly by radiation intensity and distributions of excited radicals without being destabilized. Hence, the investigation has great advantages in characterizing the structure and reaction zone of flame. Based on a bench-scale opposed multi-burner (OMB) gasification platform, a fiber spectrometer and a high-temperature endoscope coupled with a CCD camera were applied to investigate the two-dimensional distributions of OH* as well as CH* chemiluminescence of diesel and coal water slurry diffusion flames. The effects of oxy-fuel equivalence ratio and impingement on flame structure and OH* and CH* distribution were further compared. The results show that there exists OH*(306.47, 309.12nm), CH*(431.42nm), Na*(589.45nm) as well as K*(766.91nm, 770.06nm) radicals in diesel and coal water slurry flames. In addition, the peak intensity of OH* in diesel and coal water slurry flames is higher than that of CH* under the same conditions, and both decreases monotonically with the increase of equivalence ratio. As the equivalence ratio increases, the reaction zone gradually shrinks and moves downstream. Hence the flame structure and reaction zone can be characterized by OH* and CH* distribution. For one-burner diesel flame, OH* and CH* radiation distribution mainly concentrated near the burner outlet. For two-burner and four-burner impinging diesel flame, OH* and CH* radiation distribution is mainly concentrated near the burner outlet and a few in the impinging region, while it is mainly concentrated in the impinging region for four-burner impinging CWS flame. The peak intensity of OH* and CH* of four-burner impinging flame is always higher than twice the value of two-burner impinging flame, indicating that the four-burner impact is not a simple superposition of the two- burner impact. More obviously, the confining effect of impingement makes the flame lift-off length not easy to fluctuate with the change of the equivalence ratio, and the flame is always restrained near the burner outlet, which enables the combustion process to be more stable. A linear relationship between the OH*/CH* radiation intensity ratio based on the equivalent ratio and the fuel flow rate is proposed, which can be used to predict the flame equivalent ratio. This provides an intuitive and effective method for quantitatively judging the flame combustion state.

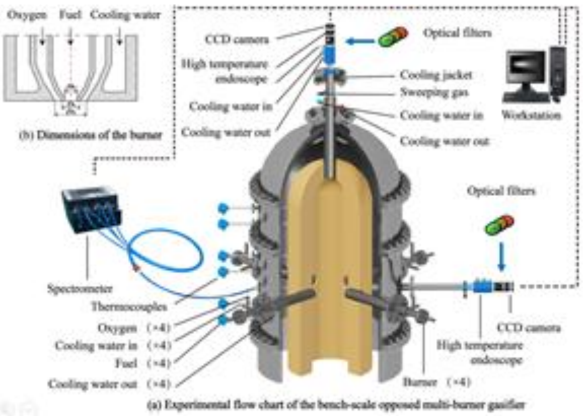

Fig. 1 Schematic diagram of a bench-scale opposed multi-burner gasifier

22.5 Influence of CaO Modified In-Situ Bio-Char on the Co-Pyrolysis of Coal and Sludge

Jiaofei Wang, Guangsuo Yu, Xudong Song, Weiguang Su, Yonghui Bai, Ningxia University, CHINA.

Co-pyrolysis of hydrogen-rich biomass and coal is the basis of co-gasification, which is one of the most important way to achieve their efficient and clean conversion. The release of biomass volatiles before coal pyrolysis causes the weakening or even disappearance of synergistic effect between biomass and coal during co-pyrolysis. Therefore, this paper intends to study the co-pyrolysis behaviors of Lingwu subbituminous (LW) and industrial sludge waste (SW) with addition of CaO, by which improves the ability of bio-char adsorbing and capturing the low temperature volatiles. CaO was physically mixed with SW, then the pyrolysis of mixture mixed with LW coal was carried out in a TG-MS. The results show that co-pyrolysis characteristic of LW coal and SW is improved by the CaO modified in-situ char. More SW and LW convert to solid, gas and tar products after the addition of CaO. The yield of gas increases but the solid and tar decrease as the CaO amount increases. It is also concluded that the addition of CaO benefits the formation of light components in tar and inhibits the production of components containing oxygen.

SESSION 23
RARE EARTH ELEMENTS III: RECOVERY OF RARE EARTHS II
Richard Winschel and Evan Granite

23.1 Developing a Mine Reclamation Approach to Recover Rare Earth Elements from Acid Mine Drainage

Chin-Min Cheng, Jeff Bielicki, John Lenhart, Professor, Tarunjit Butalia, The Ohio State University, USA.

In this study, a two-stage, trap-and-concentrate (TAC) process that uses coal combustion by-products to recover rare earth elements (REEs) from acid mine drainage (AMD) is developed. The demand of REEs (including scandium, yttrium and a group of 15 lanthanides) in making critical parts for emerging technologies is projected to grow over the coming decades. Due to the significant instability of the market, finding alternative sources has become a critical issue for the United States and other countries. In the U.S., AMD is considered a potential alternative source for REEs. When surface and/or groundwater come in contact with geologic strata containing sulfide minerals exposed by coal mining, the accelerated oxidation of sulfide minerals in the presence of natural oxidants (e.g., ferric iron and oxygen) produces sulfuric acid and promotes the weathering of the REE-bearing minerals in the host geologic strata. The TAC process developed in this study can be integrated with abandoned mine land (AML) reclamation to create an approach that can potentially provide sustainable economic incentives to restore lands adversely impacted by historical mining. This reclamation approach provides a long-term, high-volume beneficial use for coal combustion by-products, which otherwise needs to be disposed of in a landfill, to mitigate AMD discharges, remove public safety hazards, and eliminate threats to local environment and ecological systems posed by AMLs. The TAC process first uses stabilized flue gas desulfurization material (sFGD) to capture REEs from AMD (AMD REEs) and then applies a concentrating procedure to produce a feedstock that can be further economically processed to produce rare earth oxides (REO feedstock). sFGD material is a mixture of lime (CaO), calcium sulfite FGD by-product, and coal ash. The objectives of this project are to (1) validate and understand the TAC process, (2) quantify the associated economic and environmental benefits, and (3) evaluate the full-scale application potential. To achieve these objectives, tasks carried out in this project are organized into four phases. In the first phase, the research team, in collaboration with state government and private sectors, carries out a series of field investigations to screen and evaluate the seasonal variations of REEs in the AMD discharges that have high recovery potential. In addition, laboratory-scale column tests are conducted to study the trapping process under a range of percolation conditions using the AMD and sFGDs from the selected sources. Advanced analytical techniques, including synchrotron-based X-ray methods, are used to identify the controlling chemical mechanisms involved in the recovery of AMD REEs. In the third phase, a highly selective extraction procedure is used to produce the REO feedstock. Techno-economic analysis and life-cycle assessment are carried out in the final phase. Results obtained from the field investigation suggest that the concentrations of total and critical REEs in AMD have strong positive correlation with the concentrations of Al, Mn, and Si. Based on geochemical calculations, in general, trivalent ions (REE3+), monosulfate complexes (REE(SO4) +), and/or disulfate complexes (REE(SO4)2 2-) are the most dominant species of REEs in AMD. In addition, the laboratory study shows that the sFGD materials are effective in recovering REEs from AMD. Over 99% of AMD REEs that are in contact with the sFGD materials can be retained under a wide range of reaction conditions. An extraction approach has been found in this study, which is able to recover over 90% of the entrapped REEs and produce a REO feedstock that has enriched REE concentrations. The economic and environmental benefits of the TAC-embedded AML reclamation approach are also evaluated.

23.2 Recovery of Rare Earth Elements from Coal Fly Ash Leachates by Supported Liquid Membranes

Heileen Hsu-Kim, Ryan C. Smith, Mark R. Wiesner, Duke University, USA.

Coal combustion residues and other geological waste materials have been proposed as a resource for rare earth elements (REEs, herein defined as the 14 stable lanthanides, yttrium and scandium). The extraction of REEs from residues often generate acidified leachates that require highly selective separation methods to purify the REEs from other major soluble ions in the leachates. Here, we studied supported liquid membranes (SLM) as a means to concentrate REEs from coal fly ash leachates. The SLM approach relies on the sample chemical principles as the conventional solvent extraction method for concentrating REE from acidic feedstocks. In both cases, an organic solvent such as kerosene contains an REE-chelating molecule (such as di(2-ethylhexyl) phosphoric acid – DEHPA) to selectively remove the REE from the aqueous feed solution. An acid stripping solution is then used to back extract the REE from the solvent into an aqueous product solution. The SLM process is different from conventional solvent extractions in that the organic phase is impregnated into the pore space of a hydrophobic membrane, and this membrane acts as a 'filter' to selectively partition REE ions from the feed solution on one side of the membrane into the acid stripping solution on the other side of the membrane. A potential advantage of the SLM process is that it requires much less volume of hazardous organic solvents than the conventional approach and could be implemented in a modular system. The application of SLM for complex feedstocks, such as acid leachates of coal combustion resides, has yet to be comprehensively tested.

We applied a two-cell SLM reactor (16 cm2 membrane area) to test the recovery, selectivity and flux of REE from the leachates of two types of coal fly ashes and under a variety of SLM separation conditions. The recovery rate of REEs in the SLM configuration was generally slower than a conventional solvent extraction, demonstrating that improvements in mass transfer rates and membrane area are needed to achieve a scalable process. Nevertheless, a 24 h extraction by our two-cell SLM reactor was able to concentrate the leachate of a coal fly ash (originally containing 400 mg/kg total REE) to a product that contained 46,000 mg/kg total REE (or 4.6 wt% by dry mass). The SLM process was also notably more selective for the heavy (and higher value) REEs, while the conventional extraction process was more selective for the light REEs. A flux-based model of the extraction process suggests that recovery rates were limited by REE affinity for the organic chelator DEHPA in the SLM, rather than limited by REE ion diffusion kinetics as in the conventional solvent extraction approach. This model result could explain the high selectivity of heavy REE in the SLM separation, because the binding affinity of DEHPA for REE ions tend to increase with REE atomic mass. Altogether, these results demonstrate the promise and technical challenges of SLM as a new approach for concentrating REE from coal combustion residues.

23.3 Electrochemical Recovery of Rare Earth Elements from Ohio Coal and Coal By-Products

Gerardine G. Botte, Behnaz Jafari, Alamgir M. Haque, Xiang Lyu, Ohio University, USA.

The rare earth elements (REEs) are a group of 15 lanthanide elements plus Scandium and Yttrium with similar properties. REEs are strategically important as they are used in numerous technologies and applications. They are key raw material for high performance magnets, catalysts in automotive and petroleum industries, coloring of glass and ceramics, and metal alloys, to name but a few [1, 2]. Current limitations on mining and growing demand for REEs have resulted in the search for alternative REE sources and recovery methods [1].

Within the context, coal and coal byproducts have been suggested as potential sources for these precious metals. This study is meant to demonstrate the technical and economic viability of electrochemical extraction of REE from coal and coal byproducts by implementing coal electrolysis which was well studied in the Center for Electrochemical Engineering Research (CEER) [3, 4]. Results of this research will be presented at the conference.

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4.Jin, X. and G.G. Botte, Understanding the kinetics of coal electrolysis at intermediate temperatures. Journal of Power Sources. 195(15): p. 4935-4942.

23.4 Thermal Recovery of REEs from Coal Ash

Rod B. Vera, Technologies International Corporation; Howard McClintic, CTC Foundation; USA.

A novel method for recovering of REEs from coal ash using a modified electric arc furnace (EAF) to transform the organic and inorganic materials in the coal ash. This high temperature, carbothermic process reduces the metals and rare earth elements (REEs) into a misch metal. These metals can then be either conventionally processed or be recovered individually by using this high heat approach.

The production of coal combustion residues (CCRs) is an on-going problem for the U.S. electric power industry as the average power plant produces more than 540 tons per day (tpd) of CCRs. There are 676 coal ponds that are adjacent to existing coal-fired power plants and receive much of the 60 million tons that is produced annually. REEs are found in CCRs that contain significant amount of REEs.

The Technologies International Corporation (TIC) owns a carbothermic reduction process for the recovery of REEs from coal ash that was demonstrated by an earlier contract with DOE's NETL that was found to be a success. TIC is the only thermal technology for extracting REEs from coal fly ash from power plants' impoundments. Since REEs have been, are, and will be almost exclusively imported from China, it is of national strategic importance that the Nation become more self-sufficient.

A by-product of extracting REEs from coal fly ash is thermally vitrified slag. The slag is a safe and desirable aggregate for concrete.

TIC has been in existence for 10 years and holds 18 related patents. The process has zero air emissions. Nearly $9 million invested in TIC, including $1.25 million funding from DOE's NETL. This process can convert and recover the REEs in a safe, environmentally sound and cost-effective manner.

23.5 Effect of Extractive Agent and Ca Content on Extractability of Rare Earth Minerals from Ca-Rich Coal Ash

Ward Burgess, Megan Macala, National Energy Technology Laboratory and Leidos Research Support Team; Catherine Spencer, Bret Howard, Murphy Keller, National Energy Technology Laboratory; Ken Ladwig, Electric Power Research Institute; Evan Granite, National Energy Technology Laboratory; USA.

Rare earth elements (REEs) are comprised of the 15 lanthanide elements, scandium and yttrium. The National Energy Technology Laboratory (NETL) has collaborated with the Electric Power Research Institute (EPRI) to study REE extraction from coal and coal combustion byproducts. EPRI has supplied NETL with various samples of fly ash, bottom ash, ponded ash and landfilled ash. The objectives of this study are twofold: (1) to correlate the extractability of REEs to the Ca content in an ash sample, and (2) to assess the effect of acid strength on the extractability of REEs from the ashes. Scanning electron microscopy was used to study the REE distribution throughout the feed ash and residue particles. X-ray diffraction elucidated the effect of acid strength on individual mineral constituent recoveries as well as total REE recovery. Using an acid strength of 2 mol/L, up to 75% of the REEs can be recovered from a fly ash derived from combustion of a sub-bituminous coal.

SESSION 24
COMBUSTION TECHNOLOGIES I
Massood Ramezan and Johan van Dyk

24.1 Improving Coal Fired Plant Performance Using a Coal Tracker Optimization Tool

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Microbeam Technologies Incorporated (Microbeam) is currently developing and testing a tool called Coal Tracker Optimization (CTO) program. The CTO is designed to improve power plant efficiency through the enhanced prediction and control of coal properties. This paper provides an assessment of the CTO program's performance in tracking coal properties from the point of analysis to the burner. We assessed the ability of CTO-derived as-fired coal quality data to improve predictions of burner performance.

The CTO program was trained to track coal through the coal handling system at a 450-MW power plant, outputting coal properties data at the burner. The CTO program models the coal handling system which comprises a 30,000-ton live storage system and a 3,000-3,500-ton system of belts and silos. Coal properties analysis data from an online full stream elemental analyzer (FSEA) is assigned to coal as it moves into the coal handling system. Online data from the plant is used to track coal through the system. Microbeam conducted field testing to collect samples of coal at various stages through the coal handling system, from FSEA to the burner. Outputs from the CTO program were compared to coal property analysis data from samples obtained at the burner. The CTO program was optimized using data-driven methods to predict coal quality at the burner at 99.5% accuracy. Furthermore, we assessed the ability of CTO-derived as-fired coal quality data to improve predictions of burner performance by training neural networks. Burner performance predictions were carried out using Evolutionary Exploration of Augmenting Memory Models (EXAMM), an evolutionary augmenting neural network training methodology. Neural networks were developed to predict flame intensity as a function of inputs including operating parameters and coal quality parameters.

Matching coal properties with plant operating parameters improves plant performance and reliability while decreasing maintenance costs. The CTO is part of Microbeam's larger effort to develop a set of advanced tools for power plants to predict and manage day-to-day operational challenges. The CTO program enables strategies to control coal properties by tracking and optimizing as-fired coal properties for improved plant performance and reliability. Furthermore, by reducing uncertainty in near-term coal properties, the CTO program enables operations strategies which can improve efficiency and emissions but are not attempted in scenarios with uncertain coal properties.

24.2 Computational Study of Staged Pressurized Oxy-Fuel Combustion of Methane and Pulverized Coal in a Lab-Scale Reactor

Ansan Pokharel, Gideon Udochukwu, V'yacheslav Akkerman, West Virginia University; Co-Author: Pan Du, Zhiwei Yang, Richard L. Axelbaum, Washington University at St. Louis; USA.

Staged pressurized oxy-coal combustion (SPOC) is a promising technology for advanced low-cost, low-emission, high-efficiency power generation. This technology is being developed at the Washington University at St. Louis (WUSTL) using a 100kW lab-scale reactor to investigate the process experimentally. In the present study, the computational simulations performed at West Virginia University (WVU) compliment the WUSTL experimental research in order to understand the impacts of fluid flow, particle dynamics, turbulence, flame dynamics, and heat transfer. The simulations employ the species transport model with the finite rate/eddy-dissipation turbulent-chemistry interaction sub-model for coal combustion as well as the non-premixed combustion model for methane combustion. The discrete ordinates radiation model is used to account for the radiation effects. The simulations are performed for the power of 90 kW resulted from coal combustion, with varying amounts of methane addition. A small amount of the carbon dioxide (CO_2) is injected to carry the coal. Steady and unsteady Reynolds-Averaged Navier-Stokes (RANS) simulations are performed showing an asymmetric flame shape. In this respect, three causes of such a flame asymmetry are hypothesized, namely: (i) the influence of coal injection, (ii) the onset of the shear-layer instability due to various densities and velocities of the streams in a shear layer where mixing occurs and (iii) presence of the vortex shedding due to the flow past a bluff body, which is used to stabilize the flame. As a result, the impact of the presence of coal on flame symmetry is demonstrated, and a critical condition at which further increase of coal result in flame asymmetry has been found. The RANS are followed by the large-eddy simulations (LES) to be compared to the WUSTL experimental results. It is anticipated that the results of this computational study will guide the scale-up when the experimental and computational observations from the lab-scale reactor are extrapolated to a large pilot-scale reactor and, eventually, to the full-scale applications.

Acknowledgement: This work is funded by the US-China Clean Energy Research Center – Advanced Coal Technology Consortium (CERC-ACTC).

24.3 Sub-Micron Ash Aerosol Formation in Oxy-Coal Combustion at Atmospheric and Elevated Pressures,

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Pressurized oxy-coal combustion is regarded as a technology to minimize CO2 emissions with potentially improved total efficiency compared with combustion at atmospheric pressure. This work intends to understand the mechanism governing sub-micron ash aerosol formation under high pressure conditions, which has been rarely studied. Oxy-coal combustion tests were conducted on a 100 kW (rated) combustor operated at atmospheric pressure (1 bar) and a 300 kW (rated) pressurized reactor at elevated pressures (8 and 15 bar). The peak temperatures in the 1-bar and 15-bar tests were closely controlled to exclude the effect of temperature difference on aerosol formation. A high-pressure sampling system was designed and used in the pressurized tests. The particle size distributions were measured using a Scanning Mobility Particle Sizer and a Berner Low Pressure Impactor. The impactor also collected ash samples for the Scanning Electron Microscope and Energy-dispersive X-ray Spectroscopy to analyze size-segregated compositions. Results show that at similar temperature but higher combustion pressure, alkali metals are more likely to exist in the condensed phase to form fine ash particles during the vaporization-condensation process. The elevated pressure also reduces the vaporization of less volatile mineral species and causes a lower concentration of sub-micron ash aerosol.

24.4 Experimental and Computational Studies on a Mediated Oxycombustion System

Kanchan Mondal, Adam Sims, Hussein Al-Mrayatee, Bal Krishna Adhikari, Quan Zhang, Southern Illinois University, USA.

Advanced combustion systems such as oxy-combustion and chemical looping combustion are being vigorously investigated due to their promise to circumvent or reduce the energy penalty for post combustion carbon dioxide capture. Similarly coal direct fuel cells are also being investigated to increase the efficiency of electricity generation by bypassing the entropy generation issue during heat transfer in traditional power cycles. The presented approach synergistically combines the basic objectives of three such technologies, namely oxy-combustion, chemical looping and liquid anode DCFC, and transforming them into a lean, single unit process - Mediated Oxycombustion with Integrated Uncoupled Oxygen Supply (MOBIUS). In MOBIUS, the solid fuel is combusted in the absence of any nitrogen as in oxy-combustion/CLC.

However, the carbon is not combusted directly by oxygen but by a metal oxide as in a CLC. Unlike conventional CLC, the MeOx and Me in this system is in the liquid phase to improve the combustion rates and the mobility of the metal and the oxide (as with CLOU). The metal is re-oxidized at the walls of the combustor with oxygen that is uncoupled from the reactor wall material. MOBIUS incorporates innovations that overcome the bottlenecks of each of these technologies such as a) controlled combustion in a molten oxide to overcome the issues related to high temperatures (oxycombustion); b) obviating the need of solids transport between reactors (CLC) due to a single reactor system; d) improved kinetics compared to conventional CLCs for coal based systems and d) avoiding operational issues such as electrical resistance, ash separation, impurity tolerance etc. (DCFC). The subsystems for the integrated system include oxygen transport membrane, molten metal (oxidation of molten metal), and molten metal oxide (carbon combustion. The individual subsystem studies will be presented and the integration of the various subsystems into a single reactor system will be discussed. Results from the subsystem will include the combustion rates, metal oxidation rates, oxygen uptake, transport and release rates under various conditions and composition of the membrane (during the membrane evaluation).

The reactor wall material is a trifunctional oxygen transport membrane that can a) extract oxygen from air (or CO2) on the supply side, b) efficiently transport the O2- through the bulk and c) release oxygen on the reactor side. We will present experimental and computational results used for the optimization of this membrane which determines the oxygen supply rate and in turn controls the overall rate of combustion. The design of the membrane will be discussed using conductivity studies, CLC studies on the individual components and DFT studies for optimization. The overall oxygen transport rates across the membranes will also be presented.

The selected Me/MeOx is Sb/Sb2O3. This system is chosen since the melting point of Sb and Sb2O3 are within 30 K of each other and both are less than 950 K. In addition, Sb has a higher density than Sb2O3 and thus gravity can be used for the transport of the oxidized and reduced moieties. We will present the oxidation kinetics of Sb in pure oxygen and oxygen supplied across the membrane. Results from the combustion of Sb2O3 with methane and coal will be presented. Finally, the long terms operation of the integrated system will be demonstrated. In addition, multiphysics modelling (ANSYS –FLUENT) of the overall process will be presented including species distribution and temperature profiles will be provided. The impact of radiative heat transfer vs convective heat transfer will be discussed.

24.5 Influence of Coal Ash and Alkali Chloride on CuO-Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling

Jinze Dai, Kevin J. Whitty, The University of Utah, USA.

Chemical looping with oxygen uncoupling (CLOU) is considered an attractive technology for the efficient coal combustion with inherent CO_2 separation. CLOU utilizes the gaseous O_2 released from the oxygen carrier to burn the coal, producing a concentrated CO_2 stream to be readily captured. During the coal-fired CLOU process, coal ash and KCl/NaCl vapors will be generated and possibly interact with the oxygen carrier. Based on thermodynamic modeling, experiments using various reactors (TGA/fixed-bed/fluidized-bed) and coal ashes (Illinois #6/PRB/Sufco/Skyline/North River), and material characterization (XRD and SEM-EDS), the impact of coal ash and KCl/NaCl vapors on the performance of CuO-based oxygen carriers was evaluated comprehensively. The phase diagrams of simulated CuO/coal ash mixture predicted that the ash whose Al_2O_3/CaO mass ratio is greater than 1.82 may deactivate CuO by forming $CuAl_2O_4$, which does not give off gaseous O_2 spontaneously. TGA redox cycles of different CuO/coal ash mixtures indicated that the CuO deactivation is positively correlated with the Al_2O_3/CaO ratio of the ash. The addition of CaO into the risky coal ashes was found to mitigate the deactivation of CuO. XRD analysis confirmed that the added CaO consumed the Al_2O_3 that would otherwise bond with CuO by forming $CaAl_2Si_2O_8$ (anorthite), which is more thermodynamically favored than $CuAl_2O_4$.

According to thermodynamic modeling results, the interaction between CuO-based oxygen carriers and KCl/NaCl vapors could lead to the formation CuCl, decreasing the oxygen transport capacity of oxygen carriers. Around 3.5 ± 2.0% of the Cl was predicted to be converted into CuCl depending on the temperature, KCl/NaCl concentration, steam concentration, and the type of support material. The conversion of Cl into CuCl increases with increasing temperature and KCl/NaCl concentration, while it declines with increasing steam concentration. Among the common support materials, the tendency to facilitate the Cl conversion was predicted to be in the following order: $SiO_2>TiO_2>Al_2O_3$. The experimental results demonstrated the alkali chlorides notably reduced the oxygen-releasing capability of CuO-based oxygen carriers.

The fluidized-bed tests of oxygen carrier and coal ash mixtures suggested that certain coal ashes are likely to enhance the agglomeration propensity of oxygen carrier particles. Furthermore, there are three phenomena revealed by SEM-EDS and XRD analyses: 1) the migration of CuO fines from the support to ash particles, 2) the deposition of small ash particles on the surface of oxygen carrier, 3) the formation of $CuAl_2O_4$ and $CuFe_2O_4$.

On the basis of the two deactivation mechanisms described above (Al-induced and Cl-induced), a global CuO deactivation rate model has been built in this work to estimate the loss of CuO caused by the coal-derived inorganics in full-scale continuous operation units.

24.6 Characterization of Atomized Coal Slurry through Pintle Injector for Oxy-Fuel Combustion

Ana Rios, Mohieminul Khan, Mehrin Chowdhury, Ahsan Choudhuri,
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Zero-emission power sources are currently at the focal point of research in the energy sector. A practical approach is to replace the air with oxygen for the combustion process. This would reduce the production of Nitrogen and Sulphur based greenhouse gases and increase production of capturable carbon dioxide; this process is called oxy-fuel combustion. This paper presents an injection method of fluidized coal (water-coal slurry) and gaseous oxygen for oxy-coal combustion. The injector researched is a pintle injector; invented in the mid-1950's. It was primarily used for rocket and propulsion applications and ejects a reactant on an axial manner with the secondary reactant on a radial direction. When both of them collide, they form a spray that mixes and atomizes the mixture. The injector was originally used for propellants on a similar phase (i.e. liquid-liquid or gas-gas). This paper aims to present the results of coal-water slurry and gaseous oxygen atomized spray through a pintle injector. Shadowgraph techniques and high-speed recording have been used to capture droplet images. A customized software has been used to post process the images to determine the mean droplet diameter, breakup length, and spread of the droplets. The paper compares the total momentum ratio against the spray angle and the droplet size atomization of the mixture.

SESSION 25
CLEAN COAL DEMONSTRATION AND COMMERCIAL PROJECTS I
Thomas Sarkus and Alberto Pettinau

25.1 Building a Coal Based Energy System in Pakistan

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The first open pit mine is now functional at the 175-billion-ton coal deposit at Thar in Pakistan. Two coal fired power plants of 330-megawatt capacity each will come on line early this year. After ignoring this black gold for over thirty years Pakistan is now moving towards a coal-based energy system.

Ever since the discovery of huge gas reserves (12 TCF) in 1952, Pakistan has developed an extensive state of the art gas transmission and distribution network spread over 100,000 km. As the reserve is now depleted (2 TCF) the country faces serious shortfall (1200 mm cfd) which is now being met by imported Liquified Natural Gas (LNG) that costs 35% higher than local gas. Substitute Natural Gas (SNG) or shale gas can be a viable option.

In addition to domestic use the country has a huge network of Compressed Natural Gas (CNG) and fertilizer complexes that require gas. With its huge coal reserves and depleting gas deposits Pakistan now faces a challenge to build a 21st century environment friendly clean coal-based energy system. Several state-of-the-art technologies are being considered (IGCC, SNG, GTL, CTL etc.) to build an efficient network.

25.2 Making Coal Relevant for Small Scale Applications: Modular Gasification for Syngas/Engine CHP Applications in Challenging Environments

Harvey Goldstein, Senior Project Manager, Worley Group, Inc.; Charles Ward, University of Alaska – Fairbanks; Rolf Maurer, Hamilton Maurer International, Inc. – Hudson; David Thimsen, Hamilton Maurer International, Inc. – St Paul; Brent J. Sheets, University of Alaska – Fairbanks; Randy Hobbs, Hobbs Industries, Inc.; Frances Isgrigg, Russell Steiger, University of Alaska – Fairbanks; Diane Revay Madden, USDOE National Energy Technology Center; USA; Alberto Pettinau, Sotacarbo S.p.A., ITALY.

Small-scale coal gasification technology (1 to 20MWe), coupled to a reciprocating engine generator (gaseous or liquid fueled), has the potential for making coal a cost competitive resource for meeting the flexible energy needs and resiliency requirements of both industries and utilities worldwide. To maintain grid stability and reliability, electrical generation must be regulated to match the load at the proper voltage and frequency. With the expansion of intermittent sources into electrical grids, such as wind and solar, frequency and voltage regulation become increasingly important and challenging.

This work presents the results of our Front-End Engineering and Design (FEED). The FEED details the engineering and preliminary economics of a small-scale, air blown, fixed bed gasifier operating at near-atmospheric pressure (≈ 10 PSIG), with gas cleanup to provide syngas and pyrolysis liquid fuels for use in reciprocating engine generators (in the range of 2 to 10 MWe) at the University of Alaska Fairbanks. Fairbanks is a "Serious non-Attainment Area for $PM_{2.5}$", the system is designed so that emissions meet the most stringent air quality requirements in the United States.

By coupling the gasifier to a reciprocating engine, the system can be used in load following and in distributed generation applications. By modularizing the components, manufacturing costs are lowered so that syngas/engine modular systems become significantly more competitive with similarly sized conventional steam generation plants.

This technology has the potential for making coal a cost-competitive resource to meet the need for flexible, intermittent, operations that are increasingly important to electric utilities. Because steam-electric coal plants require longer periods to change their generation set points, they are less effective for providing shorter-term voltage and frequency regulation services to the grid. Reciprocating engines are capable of load acceptance and shedding rates significantly higher than steam turbine generators. With major infrastructure, coal supply, and operations already in place, existing plants currently burning coal to serve heating or power loads are logical locations for adding a syngas/engine system to provide price stable, flexible generation that responds quickly to changes in electrical supply requirements. By placing a syngas/engine system at the interface of the grid, the system can quickly respond to changes in load while the larger, steam-electric coal plant ramps up or down to meet the longer-term needs of the grid.

This FEED study presents capital and operating cost estimates defining the potential for small-scale, modular, coal gasification units to significantly reduce fuel costs from oil to coal for conventional small-scale power generation by enabling firing of reciprocating engine generators with coal-derived syngas and liquids. Gasifier automation will be key for integrating this new technology into the existing diesel plant infrastructure that is typically found in Alaskan villages and in other sites throughout the world, and for sites that have grid islanding requirements.

25.3 Ultralow Emissions for Coal Fired Power

Geoffrey D. Bongers, Gamma Energy Technology P/L; Nikolai K. Kinaev, Strategic Energy Consulting P/L; Zvonko Pregelj, Altaprom International P/L; AUSTRALIA.

The burning of coal for electrical power generation is increasingly being demonized around the world in favor of renewables despite their frailty in the absence of large-scale economic storage solutions. However, an Australian technology configuration has been identified that by a relatively simple retrofit, can reduce emissions from coal fired power stations by up to 99.8%. The technology removes SOx, NOx and practically all the particulates in the flue gas from the power station and feeds it to a slightly modified gas turbine which concentrates the CO2 and increases the net power to the grid. The increase in the concentration of carbon dioxide in the turbine exhaust in turn reduces the energy demand of downstream carbon capture thereby not only increasing overall system efficiency compared to alternative configurations that capture the CO2 from separate or combined exhaust gas streams but also reducing the size and therefore cost of the capture plant. Although the technology can be applied to new facilities its immediate benefit is seen as the acceptable prolongation of coal fired power at least in the short to medium term. In addition, since the application of carbon capture technology has been largely limited to applications such as enhanced oil recovery the additional electrical power and reduced costs of capture have the potential to increase oil recovery thus further showcasing the beneficial use of coal.

25.4 FPO Flameless Pressurized Oxy-Combustion Industrial Development Progresses, and the Projected Change of Scenario from Global Warming to Industry De-Carbonization

Massimo Malavasi, Itea S.p.A., ITALY; Richard Horner,
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Global warming significantly impacts the future of coal power prospects. Generation and de-carbonization concepts are becoming a new tide which will impact all industrial segments.

FPO technology (Flameless Pressurized Oxy-combustion) is a technology of compelling interest for coal power with CCS. Its peculiar advantages are best-in-class efficiency, flexible fuel choice, fast response to cycling, ultra-low overall emissions, positive water balance, ease in 90% CO2 recovery, and minimal posttreatment of the pure CO2 (EOR ready) output stream.

A consortium of US players – Southwest Research Institute (SwRI), ITEA (technology provider), University of Wyoming (UW), Electric Power Research Institute (EPRI), Sargent & Lundy and General Electric – is making significant advances to engineer a FPO coal power large pilot platform for the validation project. The three-phase technology industrial development program is supported by DOE funding awards. The consortium is at Phase II large pilot Front End Engineering Design (FEED) with a deadline of 2020. A schematic coal power cycle, which is under industrial development, is represented.

ITEA and UW aim to develop a full range of FPO coal power different solutions: new facility grass root CCS, ready for CCS with progressive move to CCS by adding CO2 recovery modules, and existing coal facility FPO retrofitting applications to both electrical generation and heat and power applications. Projected Levelized Cost of Electricity (LCOE) of the three solutions are represented, versus the base case technology of supercritical-pulverized coal (SC-PC).

In addition, FPO solutions for other industrial segments are at the industrial exploitation stage, like municipal waste-to-products only, with > 90% CO_2 recovery for commercial uses. Second in the line is lean gas-to energy, but with 90% CO2 for CCU. Furthermore, NG power generation with CCS, flare/lean/low BTU gas to energy with CO2 for EOR, and treatment of toxic/low rank hydrocarbon streams in CCS set up, are in the pipeline.

The above evidences are suggesting that ITEA and UW consider a new fossil energy FPO development philosophy, which sets carbon management as pinnacle objective, focusing then on a cascade of solutions tailored for diversified industrial segments, which offer a comprehensive response to de-carbonization and broad industrial issues.

25.5 Challenges of Solid Handling in Low Rank Coal Pyrolysis Pilot Testing

Cliff Y. Guo, National Institute of Clean-and-low-carbon Energy, CHINA.

Low rank coal (LRC) accounts for over 40% of the total coal reserves in China and world. The high efficiency and clean utilization of LRC plays an important role to meet the strong energy demand, reduce SOx/NOx/Hg and PM2.5 emissions. China Energy built the world first MTon scale direct coal-to-liquid (DCL) plant in Erdos, China, and operated stable since December 2008. The DCL process produced large amount of residue (DCLR). National Institute of Clean-and-low-carbon Energy (NICE) developed advanced Coal Refining (CoalRef®) technology, which can efficiently produce high value liquid and solid products from co-feeding of LRC & DCLR. The solid handling of LRC & DCLR is very challenging during the feeding and pyrolysis process and need the special care. The solid product is not only stable and has much higher heating value than the raw coals, but also has much lower sulfur and Hg content, and can be used for gasification and combustion in a much cleaner way. The valuable liquid products can be used directly or upgraded to high value fuels and chemicals. The pilot plant was built in ShaanXi Yulin of China, after many successful tests, the Coal Refining technology has been demonstrated and it shows the LRC & DCLR can be pyrolyzed together to produce valuable product.

SESSION 26
CARBON MANAGEMENT III
Bingyun Li and Fred McLaughlin

26.1 Reducing Energy Required for CO_2 Separation and Recovery Process by Employing Phase Separation Solvents

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The CO_2 separation and recovery process is known to be one of the most energy consumers in operating CO2 capture and storage (CCS). It accounts around 60% of the total cost for the CCS. The CO2 chemical absorption with a conventional amine solvent like monoethanol amine requires energy around 4 GJ/t-CO_2 recovery. Recently we developed phase separation solvent systems which consist of not only amine but also hydrophobic solvent like ether. This system, before CO_2 absorption, exhibits a single phase, while after CO2 absorption, it turns into two phases, one is CO_2 rich phase and the other is CO2 lean phase. In this study, we examined the phase phenomena for several types of amine and a hydrophobic solvent mixture before and after CO2 absorption to find a suitable phase separation solvent system to reduce the amount of the energy required for CO2 recovery. Based on the observation, the mechanism for the phase separation and solvent regeneration is studied. Furthermore, the CO2 solubilities were measured at varying temperature and CO2 pressure. It was found that the phase separation type solvent shows a larger solubility difference with a smaller temperature swing. Combined with the reaction heat recovery, the energy requirement for CO2 separation and recovery was thus estimated to be as low as 1.6 GJ/ton-CO_2 for 2-(Ethylamino) ethanol/Diethylene Glycol Diethyl Ether/Water (30:60:10 wt.%).

26.2 Modeling the Life Cycle Impacts of U.S. Coal Mining at a Regional Level

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The Department of Energy's (DOE) National Energy Technology Laboratory (NETL) uses a process-based life cycle model to account for the energy and material flows for a regionalized coal supply model. This model allows for the characterization of environmental impacts from the extraction, processing, and transportation of coal from mines to power plants. It identifies environmental reduction opportunities that can enable coal to be competitive with other energy resources on an environmental impact basis. It also establishes an environmental footprint per unit of coal for the various combinations of coal basins, mine types, and coal types, as well as a national average footprint. The key data sources for this work include power plant and coal mine receipts from Energy Information Administration (EIA) EIA-923 Data, EIA Coal Production data, Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP) data, ABB Enterprise Software (formerly Ventyx), as well as United State Geological Survey (USGS) data on water use at coal mines.

To our knowledge, this is the first comprehensive coal production model for the United States to calculate environmental impacts for different coal types, mine types, and coal basins in the United States. In theory, this model could estimate parameters for 48 combinations of coal type, mine type, and coal basin, however EIA data indicates that only 35 combinations are used in the US. The remainder of these unused combinations rely on national average values if they are called upon in the model.

This work models environmental impacts for a comprehensive life cycle inventory that is sufficiently representative to run the TRACI impact assessment method and generate comparative results. This comprehensive model is important for several reasons. First, benchmarking the impacts of coal is necessary for temporal comparisons; to gauge environmental improvements up through the present and for a reference to point back to with future improvements to the coal industry. Secondly, this work provides us with a better understanding of the environmental impacts of coal-based electricity production. This work will be used in a larger model to gauge the environmental impacts of electricity generation in the United States.

26.3 Wyoming CarbonSAFE: Establishing a Commercial-Scale Carbon Storage Complex Feasibility Study at the Newest Coal-Fired Power Plant, Dry Fork Station, Wyoming

J. Fred McLaughlin, Scott Quillinan, University of Wyoming, USA.

Recently, Wyoming has been an epicenter of carbon-focused research and is striving to be the nation's leader in applied carbon management and utilization. The foundation of Wyoming's carbon research programs is storage: it is recognized that providing validated storage sites across the State is a foundational need of regional carbon management. The most ambitious project to-date is Wyoming CarbonSAFE, funded by the Department of Energy. This project will determine the feasibility of establishing a commercial-scale (50+ million metric tons (Mt) of carbon dioxide (CO2)) geological storage complex in the Powder River Basin (PRB) in the immediate vicinity of Basin Electric Power Cooperative's coal-fired Dry Fork Station (DFS). Roughly centered around Gillette in the northeast corner of Wyoming, the PRB produces about 40% of all coal mined in the United States and is also home to existing CO2 pipeline infrastructure and oil & gas operations, including fields suitable for the use of CO2 for enhanced oil recovery (CO2-EOR). As such, the project benefits from a wealth of existing subsurface data, as well as a fossil energy-savvy population that appreciates the need for carbon capture and storage (CCS), thereby facilitating public acceptance. The project also stands to benefit from synergies created by the DFS-based Wyoming Integrated Test Center (ITC), a new test facility for researchers studying the management and utilization of CO2 emissions using a slipstream of DFS' flue gas. This summer the ITC will host researchers from the coal-track of the NRG COSIA Carbon XPRIZE, an international competition to incentivize the conversion of CO2 emissions into valuable products.

To further address feasibility a new stratigraphic test well was drilled in the immediate vicinity of DFS for the acquisition of new core (>500 ft) and geological, geophysical, geochemical, geomechanical and hydrogeological data. A new 12.25 mi2 3-D seismic survey will be conducted and paired with existing 2-D seismic data that was purchased. Comprehensive datasets of formation characteristics (e.g., permeability, porosity, injectivity, cap rock integrity) will be prepared to determine the feasibility of the potential storage units within the storage complex. Storage complex models will be calibrated and updated and revised numerical CO_2 simulation results will optimize implementation strategies. Results will help the team reduce the project's technical (e.g., number of injection wells and their placement) and nontechnical risks (e.g. area of review as it bears on pore space acquisition and liability for stored CO_2).

26.4 Quantifying Water Impacts from Thermoelectric Power Plants for US States and Counties

Joseph Chou, Derrick Carlson, Erik Shuster, National Energy Technology Laboratory, USA.

Thermoelectric power is responsible for 41% of all freshwater withdrawals in the United States (Dieter et al., 2018). Reliability for power plants responding to changes in water resource availability is a concern. A model to determine the water use for the power sector could be used to identify plants that contribute a significant amount of stress on the local water supply. The National Energy Technology Laboratory (NETL) has developed a model that analyzes EIA-860 and EIA-923 monthly generator-level data reported by facility owners water use data for thermoelectric power plants. Unique ID codes were created for each plant to group data, remove irrelevant entries, populate missing data, and correct for mismatched and duplicate EIA data. By using real data, the NETL approach accounts for operation and maintenance variations, like outages and downtime, and avoids overgeneralizing by reviewing all operating US power plants. Multiple analyses were conducted to replace outlier values with the industry average or median values based on the type of generator and cooling technology. The final NETL dataset is compared to other analyses of thermoelectric water use exist on a technology-based level. The US Geological Survey (USGS) used information on power plants to build a thermodynamically-based engineering model to calculate power plant water use (Dieter et al., 2018). The National Renewable Energy Laboratory (NREL) studied power plant water use utilizing data compiled from published literature sources (Macknick et al., 2011). NETL and USGS data points for state and county level water use were plotted against each other and showed R2 values of 0.94 and 0.74 respectively, showing relative consistency. USGS values tended to be higher than NETL model values, but both models had similar seasonal trends. 75% of the NETL monthly data points fell within the NREL ranges for each plant type (i.e., generation and cooling technology combination) and 87% fell within 100 gallons per MWh of these ranges. NETL and Argonne National Laboratory (ANL) collaborated to integrate this enhanced dataset into the AWARE-US (Available Water Remaining for the contiguous US) model to find regional water stress impacts. Aggregated water consumption was multiplied by its respective AWARE-US factor to calculate its water scarcity footprint (WSF). Results provide improved power plant-specific water profiles to assess regional WSFs. This enables modelers to better inform site specific water constraints for new energy development scenarios in the United States.

26.5 Carbon Capture Utilization and Storage Provide a New Opportunity for Fostering Cleaner and More Sustainable Energy Future – an Integrated Low Carbon Economic Development Strategy for Fossil Energy Rich Regions in Wyoming and the Ordos Basin China,

Zunsheng Jiao, Kipp Coddington, Heng Wang, Fred McLaughlin, Scott Quillinan,
University of Wyoming, USA.

The current global energy system relies on the combustion of fossil fuels to power the world economy. EIA's 2018 annual energy outlook predicted that fossil fuel sources of energy still dominate energy use in 2050. Therefore, managing CO2 emission from the utilization of fossil fuels will remain a priority for decades to come. To maintain a health and environmentally friendly energy industry future, fossil energy rich regions, such as Wyoming in the United States and the Ordos Basin in China whose economies highly depend on fossil energy, must attract innovative techniques. Such facilities and techniques are needed to effectively and efficiently continue development of vast fossil energy resources -- including coal, coalbed natural gas, natural gas, and crude, -- while reducing carbon emissions. To face these challenges, The Center for Economic Geology Research (CEGR) in the School of Energy Resources at University of Wyoming has developed an integrated energy/CCUS development strategy, which aims to synchronously, systematically integrate existing and create new industries -- developments of the coal mining, coal conversion industry, coalbed methane production (CBM), CO2 enhanced oil recovery (CO2 EOR), enhanced water recovery (CO_2 EWR), and CO_2 geological storage in the Powder River Basin, Wyoming, and the Ordos Basin, China.

In this systematic approach strategy, a contentious challenge associated with the development of one resource becomes part of a useful resource for the development of another. This integrate energy development strategy includes (1) coal mining would continue using existing extractive technology, or improved technology; (2) the new coal conversion facilities are located as close to the mines as possible; (3) the depleted oil/gas fields and saline aquifers would initially be used as captured CO2 reservoir and surge tanks; (4) coupling CO^2 EWR and treatment for active reservoir pressure management and water beneficial uses; (5) water produced with coal bed methane production and displaced water from the CO2 storage would be monetized and used to support the coal conversion industries; (6) CO2 stored in the surge tanks would be used to support CO2 EOR activities; and (7) CO2 would be permanently stored in depleted gas/oil and saline reservoirs.

One of the greatest strengths of this integrated systematic approach is the cost advantage and sustainable. The overlapping development of relatively new coal conversion industries with existing oil and gas industries in the Northern Shaanxi Province has created a unique opportunity to apply the systematic approach developed in Wyoming. In this study we present the results of the CO2 life cycle analysis. This study estimates that by implementation of the integrated strategy roughly 1.6 Gt of CO2 would be redirected from the atmosphere and safely stored in the subsurface, while creating new uses for local coal. Total oil production would increase, too. Approximately 430 Mt of oil could be recovered if sources of CO2 currently emitted from Coal conversion plans were capture. Lastly, we suggest that the implementation of the plan would increase the sustainability of fossil fuels in these areas while adding additional tax revenue.

SESSION 27
COAL SCIENCE III: TRACE ELEMENTS AND PYROLYSIS
Allan Kolker and Atsushi Ishihara

27.1 Thermal Desorption of Mercury and Sulfur from Coal using Spouted Bed Reactor

Quang Truong, Srujan Rokkam, Advanced Cooling Technologies, Inc.; Carlos Romero, Zheng Yao, Lehigh University; USA.

Coal naturally contains Mercury and Sulfur, which are extremely toxic in certain chemical forms. Thermal desorption is a cost-effective pre-treatment technique to remove such volatile contaminants from coal. In this work, thermal desorption of Mercury and Sulfur from coal was investigated. The coal sample was Bituminous at moisture content of 10%, and average size of 4 mm. To establish optimal operating conditions for thermal desorption of coal, reactive-CFD studies were performed using MFiX software. Experimental testing was undertaken to investigate the thermal desorption process and effectiveness of removing multiple contaminants. The experimental results show a reduction of 37% of mercury content and 15 % of sulfur content using standard spouted bed design, as well as a reduction of 65% of mercury content and 28% of sulfur content using optimized spouted bed design. This work was funded by Department of Energy SBIR Phase I program, Award Number DE-SC0017232, awarded to ACT, Inc.

27.2 Heterogeneous Microscale and Nanoscale Arsenic and Selenium Speciation in Coal Fly Ash

Heileen Hsu-Kim, Nelson A. Rivera, Duke University, USA.

Coal fly ash and other coal combustion residues (CCRs) are known to be enriched in arsenic (As) and selenium (Se). These elements can be a concern during the handling, disposal and reuse of CCRs. Both elements can be harmful to wildlife and humans if mobilized at concentrated quantities into water and soils. The extent of Se and As mobilization depends on the amount in the original ash as well as the chemical form of these elements and environmental conditions (e.g. water chemistry, redox conditions, soil surface chemistry, hydraulic conductivity). Previous research has shown that arsenic occurs mainly as the pentavalent As(V) (e.g. arsenate) in coal fly ash while selenium occurs as a mixture of oxidized Se(IV) (i.e., selenite) and elemental Se(0). However, more precise information about the chemical forms and modes of incorporation has yet to be fully elucidated.

Here, we used novel synchrotron X-ray absorption spectroscopy techniques to examine the various chemical modes of occurrence for As and Se in several coal fly ash samples generated from western sub-bituminous Powder River Basin and eastern bituminous Appalachian Basin coals. We compared elemental mapping and speciation at the nano-, micro-, and bulk-scales as a means to understand the chemical forms as well as mass distribution of As and Se within individual fly ash grains. The results of these analyses generally showed high degrees of heterogeneity for As and Se species in fly ashes and also uneven mass distribution within individual ash grains. For example, bulk scale analyses showed that As exists primarily as arsenate As(V) (80-85%), and reduced valence species (As-sulfides, arsenite) as minor forms in a subset of samples. In contrast microprobe and nanoprobe element mapping indicated that As resides in distinct domains as opposed to being diffusely distributed throughout the fly ash matrix. For example, for a Power River basin coal fly ash, arsenate As(V) was dominant in one 2 μm spot, while in another spot 80% of the arsenic is a chemically reduced form, most likely As-sulfides. The chemical speciation of selenium in coal fly ash can be even more variable than arsenic. Bulk sample analysis showed that coal fly ashes contained a mixture of selenite Se(IV) (60-100%) and elemental Se(0) (0-40%). The relative percentages of these forms varied with the type of fly ash. Micro- and nanoprobe analyses also demonstrated heterogeneities at the micron and nanometer scale for selenium species. For example, for the Appalachian Basin coal fly ash, selenium is mostly in the oxidized form Se(IV), but widely different speciation and mass distributions of Se(IV) and Se(0) were observed on two different individual ash grains.

While the exact As and Se associations within the fly ash solids has yet to be precisely determined, this work provides clues that might improve our understanding of the chemical modes of occurrence. For example, arsenic extended X-ray absorption fine structure analysis indicated the lack of second-shell backscattering atoms coordinated to As(V), unlike the spectra for our sorbed As-iron oxide reference compound that have prominent second-shell backscattering atoms (i.e. As-Fe interactions). This result suggests that in coal fly ash, arsenic probably is not solely associated Fe-oxides nor incorporated into an iron oxide crystal structure. Arsenic could be bound in other ways as well, including association with low mass elements such as Al and Si (in aluminosilicates), or incorporation into secondary phases such as calcium arsenates. The diversity of As chemical forms and mass distribution within coal fly ash particles has great implications for leaching. Environmental processes that promote dissolution of Fe-bearing minerals (e.g. such as low redox conditions) would also promote release of sorbed As forms. Oxidation state information is important because in the case of selenium, Se(IV) is more water-soluble and therefore more bioavailable than reduced species of Se(-II, 0, II). Arsenate As(V) oxyanions tend to be less mobile than arsenite As(III) forms in the aquatic environment. Altogether, these findings demonstrate the large variety of arsenic and selenium forms in fly ash particles and that predictive models for leaching of these elements should account for this complexity.

27.3 A Study of Mercury and other Trace Metals in Pyrite from Illinois Basin Coals Using LA-ICP-MS

Clint Scott, Allan Kolker, U.S. Geological Survey; Liliana Lefticariu, Southern Illinois University; Maria Mastalerz, Agnieszka Drobniak, Indiana University; Alan Koenig, U.S. Geological Survey; USA.

The U.S. EPA Mercury and Air Toxics Standards (MATS) were developed in 2011 to limit air emissions of toxic substances, such as trace metals and acids, during coal combustion. To facilitate compliance, we initiated a study focusing on the occurrence and distribution of sulfur, Hg, and other trace elements limited by MATS (e.g., Cr, Mn, Co, Ni, and Pb) in coals from the Illinois Basin. Preliminary results (Kolker et al., 2018, PCC), indicated that coal processing to reduce mineral matter and thus increase heating value had the ancillary benefit of reducing the concentration of sulfur and trace metals in the clean coal. Statistical analysis of the correlations among the bulk concentrations of organic sulfur, pyrite sulfur, and trace metals indicated that pyrite was the primary host for Hg and many other trace metals in Illinois Basin coal. However, bulk chemical analysis did not allow for detailed information/of trace metal concentration and the spatial distribution within the pyrite at the microscale.

For this phase of the study, we used laser ablation ICP-MS (LA-ICP-MS) to measure the concentration of Hg and other trace metals in pyrite from Illinois Basin coals. Our study aims to answer two questions. First, what fraction of bulk mercury and trace metal abundances are associated with pyrite? Second, to what degree does geography control the concentration and distribution of Hg and other trace elements. To this end, we selected a sub-set of 20 coal samples from the previous study for LA-ICP-MS analysis. We selected samples that included multiple raw-clean coal couplets, multiple coal beds, and that were deposited across the basin. Our results demonstrate that Hg is present in pyrite at concentrations typically in the low ppm range and can reach tens of ppm. Other trace metals (e.g., Zn, Co, Pb) range from 10s to 1000s of ppm. There is little variation between the trace metal concentrations of the raw-clean couplets, and we found no clear geographic control on the concentration of trace metals. Due to variability of trace metal content of pyrite on a grain scale, quantification of the proportion of trace metals in pyrite, relative to trace metals in the whole coal, is difficult to determine precisely. However, estimates of the fraction of bulk trace metals found in pyrite can be obtained by comparing our LA-ICP-MS results to the trace metal concentrations required if pyrite accounted for various proportions of total trace metals in coal. Using this approach, analyses on a fine scale (18 to 25 um spot size) help show the extent to which pyrite controls the distribution of elements of environmental interest such as mercury.

27.4 *In-Situ* Analysis and Theoretical Study of Vacuum Pyrolysis of N-Benzylaniline with Time-Of-Flight Mass Spectrometry

Fanggang Liu, Gang Li, Haoquan Hu, Dalian University of Technology, CHINA.

Pyrolysis of N-benzylaniline was carried out below 50 Pa from 573 to 1473 K. Vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry with molecular beam sampling was used to investigate the pyrolysis process. Nine pyrolysis species were observed. The relative concentration of pyrolysis species were estimated by semi-quantitative analysis method. A subtle change of parent structure happened at low temperature. The thermal molecular rearrangement of N-benzylaniline takes place firstly. 9,10-dihydroacridine is formed from the migration of benzyl group and cyclization reaction. N-benzylaniline starts to break up into benzyl and anilino radicals after 973K. C7H6 fulvenallene is a vital intermediate in the subsequent decomposition of benzyl radical. The theoretical calculation supports partial experimental results.

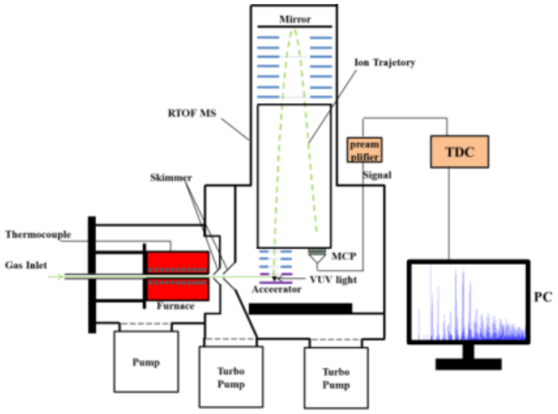

Figure 1. Schematic diagram of Py-VUV-SPI TOF-MS

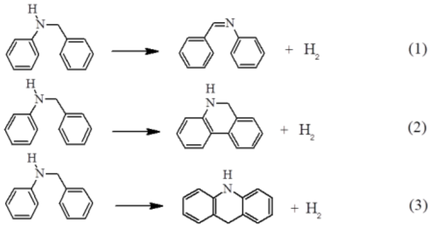

Table 2. List of major species measured in the pyrolysis of N-benzylaniline

m/z	formula	Species	T_F(K)	C_M	T_M(K)
65	$C_5H_5\cdot$	cyclopentadienyl	1173	0.181	1473
80	$C_5H_5CH_3$	methyl cyclopentadiene	1173	0.038	1473
91	$C_6H_5CH_2\cdot$	Benzyl	973	0.380	1473
92	$C_6H_5NH\cdot$	Phenylamino	973	0.054	1373
106	$C_6H_5CNHCH_2\cdot$	N-methyleneaniline	973	0.267	1273
181	$C_{13}H_{11}N$	Dibenzo tetra hydropyridine Benzalaniline	573	0.660	973
182	$C_{13}H_{11}N$	isotope peak	573	0.138	973
183	$C_6H_5CH_2NHC_6H_5$	N-benzylaniline	-	0.814	573
184	$C_6H_5CH_2NHC_6H_5$	isotope peak	-	0.134	573

SESSION 28
VALUE-ADDED PRODUCTS FROM COAL III
Kanchan Mondal and John Duddy

28.1 Large Scale Synthesis of Coal-Derived Carbon-Based Nanomaterials

Viet Hung Pham, Congjun Wang, Jennifer Weidman, Yuan Gao, National Energy Technology Laboratory, Leidos Research Support Team; Christopher Matranga, National Energy Technology Laboratory; USA.

Carbon based nanomaterials (CNMs), such as graphene nanoplatelets, graphene oxide and graphene quantum dots, have attracted attention due to their exceptional mechanical, electrical, thermal, chemical, and optical properties which make them promising candidates for applications including energy storage materials, catalysis, composite manufacturing, sensor devices. Despite this potential, the commercialization of CNMs are limited due to the expense associated with feedstock and processing costs. Domestic coal is an abundant low-cost alternative feedstock and can easily be converted into CNMs with inexpensive chemical/physical processing. In this study, we utilize mechanical exfoliation and chemical oxidation processing for the large-scale synthesis of CNMs using sub-bituminous, bituminous, and anthracite coal feedstocks. Additional chemical and physical processing allow us to control the size of the CNMs, the O/C ratio, and the general solubility of CNMs in various solvents and composite matrices. The properties of CNMs were characterized by TEM, SEM, XPS, XRD, TGA, Raman, BET, and FTIR.

28.2 Recovering Semi-Coking Wastewater by Formaldehyde-Based Phenol Extraction

Yali Wang, Jiajia Peng, Shuai Cao, Hua He, Yufei Wang, Long Yan,
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Located in the Loess Plateau, the northern Shaanxi region is rich in coal, which exceeds 280 billion tons. A large amount of coal is used to produce semi-coke, which is widely used in the production of calcium carbide, ferroalloy, ferrosilicon, silicon carbide, and other products. However, semi-coking wastewater contains a large amount of ammonia and phenolic substances, and the Chemical Oxygen Demand (COD) inside is extremely high, which is very difficult to handle and limits the development of the semi-coking industry. In the current work, these phenolic substances in the semi-coking wastewater are removed through preparation of phenolic resin by adding formaldehyde. Under the catalysis of ammonia aqueous solution, the phenolic substances in the wastewater streams are removed for recycling these water resources. The effects of pH, temperature, time, and formaldehyde concentration during reaction on the quality and quantity of phenolic resin are investigated and optimized by response surface methodology. COD and ammonia nitrogen value are detected in the reaction filtrate obtained under the optimum conditions. The content of phenolic substrate and formaldehyde in the semi-coking wastewater before and after treatment is determined by using UV-visible spectrophotometer. The individual phenolic resin is prepared for the most representative five phenolic substances in the semi-coking wastewater (phenol, m-cresol, 2,3-dimethylphenol, catechol, and 2,6-dimethylphenol) under the original and optimized wastewater treatment conditions and is characterized by in-situ infrared and thermal analysis. Thermogravimetric analysis suggests that the reaction is a two-step reaction; the water in the resin evaporates at the beginning of the pyrolysis process, then the resin is further condensed. Subsequent heating produces significant thermal decomposition of the phenolic resin with the largest mass loss followed by the final stage of pyrolysis. The types and properties of phenolic resins prepared with different phenols are unqiue, and the activation energy of the phenolic resin for phenol, m-cresol, 2,3-dimethylphenol, catechol and 2,6-dimethylphenol decrease consecutively, allowing the reaction to occur more easily. The reaction of formaldehyde with phenolic substrates greatly reduces the phenolic substrate in the semi-coking wastewater, which not only resulted in successful recovering semi-coking wastewater, but also preparing a large quantity of phenolic resin.

28.3 Selective Oxidation via Engineered Core@Shell Catalysts: Principle and Application to Dehydrogenation of Ethane to Ethylene

Yahui Yang, Eyram Akabua, Götz Veser, University of Pittsburgh, USA.

The emerging ability to engineer materials on the nanoscale promises to enable precise tailoring of materials functionality. In particular core@shell nanomaterials have gained interest in this context, as they offer interesting functional properties with application in a wide range of technologies. From a reaction engineering perspective, core@shell nanocatalysts constitute “nanoreactors” with porous membrane walls which could enable preferential diffusion of molecules and thus tunable selectivity by structural tailoring of the shell.

Using metal(oxide)@silica core@shell catalysts we are demonstrating that porous silica shells indeed allow differentiation between hydrogen and hydrocarbons in oxidation reactions, and then apply this principle to the selective oxidation of hydrogen in the homogeneous ethane dehydrogenation reaction. By carefully controlling the thickness of the silica shell with near nanometer precision via adjustment of synthesis parameters, we demonstrate control of the degree of preferential diffusion and thus selective conversion of hydrogen. C2H6 pulse experiments at 800oC show gradual consumption of lattice oxygen in Fe2O3@SiO2 catalysts, and noticeably reduced H2 and CO2 formation as well as increased olefin formation in comparison to a conventional Fe2O3/SiO2 reference catalyst.

Such core@shell materials hence open a relatively straightforward and rationally predictable approach towards designing selective catalysis based on well-established and emerging nanostructuring approaches.

28.4 Conversion of Alkylphenol to Phenol over Hierarchical ZSM-5 Zeolites: Effects of Mesoporosity against the Deactivation

Ting-sheng Chen, Zhen-yi Du, Wen-yi Yang, Di Liu, Jie Feng, Wen-ying Li,Taiyuan University of Technology, CHINA.

Fossilized and raw lignocellulose-derived phenols are generally mixtures substituted with short alkyl substituents. It is difficult and uneconomic to separate out pure products by traditional separation techniques such as distillation, since the boiling points of these alkylphenols are quite close among each other. Alkylphenols can be highly selectively converted to phenol over the ZSM-5 zeolite because of its special pore structure favoring shape selectivity. The bottleneck of dealkylation over ZSM-5 is the fast deactivation due to coke formation. In this work, a series of ZSM-5 with different degrees of mesoporosity were prepared by post-synthesis desilication with NaOH and NaOH&TPAOH solutions. The results showed that desilication with NaOH&TPAOH enabled the formed mesopores with more uniform and narrower porosity. Additionally, the zeolite catalysts enhanced the accessibility of acid sites and slowed deactivation by introducing mesopores. The fresh and used catalysts were characterized with thermogravimetry, N2 adsorption and FT-IR measurement. For post-synthesis samples, more coke formed on the external surfaces than the untreated samples, which were attributed to the mesopores that facilitate diffusion of molecules in zeolite structure. Internal coke covered more acid sites and was more likely to block microchannels than external coke, leading to a more severe deactivation.

28.5 Synthesis of Formaldehyde from Syngas via Catalytic Condensation in Functionalized Metal Organic Frameworks

Lin Li, Sen Zhang, Jonathan Ruffley, University of Pittsburgh; Kushantha Withanage, Juan Peralta, Koblar Jackson, Central Michigan University; Karl Johnson, University of Pittsburgh; USA.

Formaldehyde is a highly desirable platform chemical with an annual demand of over 30 mega tons. The current way of generating formaldehyde industrially is energy intensive, with 57% exergy loss, and uses methanol as the feedstock. The methanol used is typically produced by the oxidation of methane to syngas, followed by the reduction of CO to methanol via Fischer-Tropsh synthesis. In this work, we will present a more efficient pathway for converting CO to formaldehyde in Metal Organic frameworks (MOFs) by incorporating Lewis pairs (LPs). Here, we apply process intensification and combine catalysis with separation. This design not only overcomes the equilibrium limitation of gas phase synthesis of formaldehyde by making the overall reaction non-reversible, but also replaces costly distillation with condensation.

MOFs are a class of porous materials having potential for both gas adsorption and catalysis. Functionalization of MOFs with catalytic moieties, such as LPs, results in heterogeneous catalysts with active sites similar to those of molecular catalysts. Based on our previous studies, the one of the biggest advantages of using LPs as hydrogenation catalyst is the fact that LPs are good at heterolytic hydrogen dissociation. We have investigated the proposed pathway in gas phase, inside functionalized UiO-67, and on a freestanding fragment containing the LP (N-BF2). We found that the poisoning of the LP by CO is reduced when the LPs were incorporated into the MOF. The rate-limiting step is the hydrogenation of CO, with a barrier of 1.30 ± 0.15 eV, an improvement of 2 eV relative to the uncatalyzed reaction. We believe that conversion of CO to formaldehyde could be further enhanced in MOFs due to the increase in effective pressure inside confined pores. Additionally, this confinement effect also reduces translational degrees of freedom, which makes the free energy of the overall reaction more favorable.

The density functional theory (DFT) results presented here were primarily calculated using the GPAW code, with the BEEF-vdW functional to describe the exchange correlation energy. Using the BEEF ensemble, we also quantified the uncertainly associated with each DFT calculation due to the choice of exchange-correlation functional. Since DFT calculations for transition states are susceptible to self-interaction error, we have used FLOSIC calculations to quantify the extent of this error in our system. In addition, we also compare our DFT results with high-level ab initio methods to show that direct hydrogenation of CO to formaldehyde is promising on LPs and kinetically unfeasible absent of a catalyst for both forward and reverse reactions.

SESSION 29
COMBUSTION TECHNOLOGIES II
Evan Granite and Francis Lau

29.1 Control Scheme to Optimize Fluidized-Bed Combustion Sulfur-Capture Systems Through Integration of Fuel Properties

David Stadem, Steven Benson, Shuchita Patwardhan, Microbeam Technologies, Inc., USA.

Control algorithms were developed to optimize sulfur capture systems operations in a fluidized-bed combustion (FBC) boiler based on fuel properties and operating conditions. This algorithm utilizes mechanistic sulfur capture model that considers the varying properties of coal as it is delivered to the plant. The control algorithm utilizes a number of variable inputs to calculate the required limestone feed rate. Inputs are derived from a combination of real-time plant measurements (e.g. material flow rates or temperature) and/or manually inputted parameters (e.g. material analysis results). The algorithm utilizes a literature-aided mass-balance model incorporating mechanistic reactions between various components in the fuel and bed materials such as alkali and alkaline-earth metals (Na, Mg, K, Ca), sulfur, and alkali “getters” (Al, Si). Coals such as lignite and subbituminous coals that contain high levels of inherent alkali and alkaline-earth metals are known to contribute to sulfur capture in the bed (inherent sulfur capture). The reactivity of inherent coal elements and added limestone with fuel sulfur is incorporated into the model as a function of temperature distribution. The algorithm outputs the mass flow of limestone required to capture sufficient sulfur to meet emissions targets. The model is modularized, allowing for the addition of alternative reaction pathways, material recycle and makeup streams, reactions over time, and capture systems. In particular, we concurrently optimize operations of a combined in-bed and dry scrubber sulfur capture control scheme. The mechanistic model was empirically adjusted by reviewing historical boiler performance data, and by completing a multi-week field test to validate the mechanistic relationships between limestone addition, fuel properties, temperature, and emissions. Further, the model underwent a 1-month trial period during which additional empirical adjustments were made in order to optimize performance. Subsequently, the model was installed for online control of limestone addition rate. The algorithm demonstrates improvement over basic control schemes by identifying the lowest cost option for emissions control under multiple operating conditions. Using this algorithm, limestone addition rate is optimized according to changing process conditions. The plant is thereby equipped to minimize costs while achieving emissions targets.

29.2 The Use of Gaseous Metal Oxide as an Oxygen Carrier in Coal Chemical Looping Combustion

Quan Zhang, Debalina Dasgupta, Kanchan Mondal, Southern Illinois University, USA; Minhua Zhang, Tianjin University, CHINA; Tomasz Wiltowski, Southern Illinois University Carbondale, USA.

Traditional chemical looping technologies utilize solid oxygen carriers and have some disadvantages, especially when solid fuels like coal are used. The authors proposed a novel chemical looping process named Gaseous Oxide Assisted Looping (GOAL), in which a gaseous metal oxide is used as the oxygen carrier. Compared to traditional chemical looping techniques, GOAL offers many advantages including simplified ash separation, high oxygen carrying capacity, extended oxygen carrier lifespan, and fast reaction with solid fuels. Much progress has been made since the concept was first proposed. In this work, one of the candidate materials as the oxygen carrier was studied with a combined experimental and computational approach. The reaction of charcoal with a gas-phase metal oxide was studied for the first time. The experiments were conducted isothermally at different temperatures in a fixed-bed reactor. The apparent activation energy of the reaction was calculated, and suitable kinetic models were determined. To further investigate the reaction mechanism and determine the main reaction product, the adsorption of a metal oxide cluster on a charcoal surface and subsequent generation of COx was studied by density functional theory (DFT) method. A comprehensive analysis of plausible reaction pathways of CO and CO2 generation was conducted. The energy barriers of COx formation were obtained, and the primary product was identified. The DFT result accounts for key experimental observations of activation energy and product selectivity. The adsorption and dissociation of O2 on the reduced oxygen carrier surface were also studied by DFT method. The stable adsorption sites and possible surface reconstruction were predicted, and the adsorption energy of oxygen on the surface was calculated. The energy barrier of O2 dissociation on the oxygen carrier surface was obtained from the potential energy surface. Overall, the selected candidate was demonstrated to be a capable oxygen carrier for GOAL. This research is also an important complement for systematic investigations of carbon-metal oxide cluster interactions. DFT method was proven successful in such a system and could be a useful tool in predicting the reactivity of new oxygen carriers.

29.3 Water Utility Lime Sludge Reuse for Flue Gas Desulfurization

Justin Mock, Hafiz Salih, University of Illinois at Urbana–Champaign; Craig Patterson, U.S. EPA; Seyed A. Dastgheib,
University of Illinois at Urbana-Champaign; USA.

There are hundreds of water utilities across the U.S. that generate significant amounts of lime sludge as a result of the water lime softening process. Beneficial use of the lime softening sludge is a sustainable solution to the current landfill disposal practice. We have recently evaluated the feasibility of utilizing lime sludge in the flue gas desulfurization process of coal-fired power plants.1,2 A supply-demand evaluation showed that the water treatment plants in the U.S. generate approximately 3.2 million tons of lime sludge per year at an estimated disposal cost of approximately US$90 million. Furthermore, power utilities are using approximately 6.3 million tons of limestone per year. A life cycle assessment study showed that the environmental impact of lime sludge utilization in power plants was two orders of magnitude lower than that of the landfill disposal option. We further performed laboratory-scale studies using a simulated flue gas at a flow rate of ~0.5 LPM to evaluate performance of several lime sludge samples for SO2 capture, while investigating the mercury re-emission during the scrubbing process. Results indicated that all tested lime sludge samples, at doses less than the dose of a baseline limestone sample, reduced the SO2 concentration from 2,000 to less than 0.5 ppm. Furthermore, tested lime sludge samples exhibited lower or similar mercury re-emission compared to the limestone sample.

We have further validated our recent laboratory-scale work by performing additional experiments using a small prototype scrubber at a flue gas rate of 5-10 LPM. Several experiments were performed to test two lime sludge samples and a baseline limestone sample using a simulated flue gas containing 2,000 ppm SO2. Similar to the previous smaller scale experiments, the SO2 removal and mercury re-emission profile were monitored during the scrubbing experiments. Overall, the data trends observed for the small prototype tank scrubber are in good agreement with the trends observed for the laboratory-scale experiments. Work is in progress to perform field-testing of selected lime sludge samples for desulfurization of 5-10 LPM flue gas, obtained as a slipstream from the exhaust duct of a coal boiler at a local power plant.

29.4 A Parametric Exploration of MILD Coal Combustion

James C. Sutherland, Hang Zhou, Joshua McConnell, University of Utah, USA.

Moderate or Intense Low-oxygen Combustion (MILD) is a promising combustion technology with high efficiency and low emissions that has attracted increased attention in recent years. It has been shown that well-mixed reactants are required to reach MILD combustion regime, which can be difficult to achieve with pulverized coal. New criteria need to be tested for MILD coal combustion.

We have previously observed that scalar mixing time scale and turbulence dissipation rate are good criteria for characterizing MILD coal combustion over a range of recirculation rates and turbulence intensities. In this study, these criteria are used to test the necessity of well-mixed reactants around particles to achieve MILD combustion. Calculations are carried out using the well-stirred reactor model (WSR) and the one-dimensional turbulence model (ODT). For the WSR model, conditions to reach MILD regime are obtained based on the definition of MILD. However, the WSR model is unable to resolve spatial and temporal variations in the thermochemical state and flow field of the system. ODT calculations are used to gauge the importance of transient phenomena such as diffusive and convective mixing as well as chemical kinetics. Additionally, ODT allows us to tractably perform combustion simulations with detailed finite rate chemistry as well high-fidelity models for coal physics, which is required to obtain an accurate estimate of the NOx concentration.

Calculations are performed over a range of recirculation rates, particle sizes, and equivalence ratios for two coal types. The effect of equivalence ratio and particle size distribution on ignition delay is examined, which is compared with the scalar mixing time scale. We also consider the effect of MILD coal combustion on NOx emissions.

SESSION 30
CLEAN COAL DEMONSTRATION AND COMMERCIAL PROJECTS II
Alberto Pettinau and Thomas Sarkus

30.1 Catalyst-promoted Solvent is the New Pathway to Reduce the Cost of CO_2 Capture from Coal Flue Gases

Ahmed Aboudheir, President, Aboudheir Consulting Ltd; Maohong Fan, University of Wyoming; USA.

Carbon dioxide (CO_2) capture from coal power flue gases using amine-based solutions is a proven technological approach which has been practiced in operation for many decades. The first 800 TPD CO_2 capture plant is still in operation by Sealers Valley Minerals (SVM) for more than 40 years in Trona, California, USA. This plant is based on a conventional process configuration and uses 20 wt% mono-ethanolamine solution (MEA) to capture CO_2 from flue gases, which is used as a raw material to produce Soda Ash. The main disadvantage of using a highly reactive primary amine such as MEA is the high reboiler energy required to strip the CO_2 from the solvent.

In the last two decades, many formulated solvents have been developed, which are based on mixing primary, tertiary, and/or sterically hindered amines in order to reduce the reboiler energy demand and the expense of large absorption equipment and complex process configurations. The most recent and largest CO_2 capture plant - the Petra Nova project located in Houston, Texas, USA uses a formulated solvent to capture CO2 from coal fired flue gas at a rate of about 5,000 TPD of CO_2 for enhanced oil recovery applications.

The remaining main challenges for amine-based technologies is to reduce the absorption column size, to simplify the process flowsheet, and to reduce the reboiler heat for CO_2 stripping. The University of Wyoming has developed a nanostructured $TiO(OH)_2$ catalyst additive for amine-based solvents in order to increase the rates of CO_2 stripping from the rich CO_2 solvent stream. The laboratory CO_2 absorption/desorption behavior has been shown to be enhanced in the presence of the UW catalyst-promoted MEA solvent, with a noted marked reduction in the striping temperature than experienced for existing commercial CO_2 capture plants operating on MEA alone. These main findings contribute to simple process flowsheet, smaller equipment size, and less energy requirement for CO_2 capture from coal flue gases.

To predict the effect of the potential saving on the capital and operation expenditures of the large CO_2 capture plants, a rate-based modelling approach has been used to design a 5,000 TPD CO_2 capture plant based on coal-fired flue gas streams and a 90% CO_2 recovery rate. Based on the results of the experimental and the modeling work, it can be concluded that the use of the UW catalyst-promoted MEA solvent can contribute significantly to the CAPEX/OPEX reduction in the following main areas of the CO_2 capture process: (1) smaller absorption columns because the presence of the catalyst in the presence of a highly reactive amine-based solutions, enhances the CO2 absorption rate, reducing the need to use intercoolers/liquid redistributors within the absorption column; (2) simplifies the process flowsheet by eliminating any need for heat integrations within the CO_2 capture process; (3) lowers heat duty requirement to strip the CO_2 from the rich solvent because of using the nanostructured $TiO(OH)_2$ as a catalyst.

30.2 Preliminary Study on Civilian Clean Briquette Production by Integrating with the Surplus Capacity of Power Plant

Haohua Gao, Wandou Du, National Institute of Clean-and-Low-Carbon Energy, CHINA.

Civilian bulk coal combustion is one of the important sources of air pollutions in China, so the cleanliness of civilian bulk coal is urgent. Recently the promotion and use of civilian clean briquette are facing many challenges, among which the government's high subsidy burden is one of the key issues. Most coal-fired power plants have low load rate, resulting in a large amount of surplus capacity. Therefore, this paper puts forward the process of utilizing the surplus capacity of power plant to solve the problem of cleanliness of civilian bulk coal. The preliminary research results show that it is technically and economically feasible to use the high temperature flue gas of coal-fired power plant boilers as heat source for coal pyrolysis. This paper also gives the policy suggestions of this model, which is through the joint promotion of civilian clean briquette by large coal-fired power enterprises and the government to reduce the government burden and benefit the people.

30.3 Performance and Integrated Operation at the Kemper IGCC Facility

Matt Nelson, Pannalal Vimalchand, WanWang Peng, Southern Company; Bruce Harrington, Mississippi Power Company; Tim Pinkston, Southern Company; Diane Madden, U. S. Department of Energy, National Energy Technology Laboratory; USA.

The Kemper County IGCC Project has demonstrated lignite gasification at a 2-on-1 Integrated Gasification Combined-Cycle (IGCC) facility located in Kemper County, Mississippi. Kemper was the largest IGCC project in the world and the first to use lignite as fuel, as well as the first to capture and sell CO2. While the gasification operations of the plant have been suspended, the plant operated for over 200 days of successful lignite gasification, gathering valuable data useful for future development and applicable to a wide range of industrial applications and technologies.

Kemper featured air-blown Transport Integrated Gasification (TRIG™) technology that centers around the Transport Gasifier—a pressurized, circulating fluidized bed unit that features high riser densities and high solids circulation rates. Other unique components of the technology are the Pressure Decoupled Advanced Coal feed system (PDAC) and the Continuous Fine and Coarse Ash Depressurization systems (CFAD and CCAD). These innovative systems were developed by Southern Company, along with other industrial and institutional partners, at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama over a period of 20 years. Each train at the Kemper IGCC project represented a scale-up of the PSDF pilot plant by a factor of about 100 in terms of capacity, with each of the two Transport Gasifiers at Kemper having a feed capacity of 5,000 tons per day.

Other technologies integrated and tested on a commercial scale at Kemper include syngas filtration, acid gas removal, and hydrogen-rich low Btu syngas combustion. The Particulate Control Devices (PCDs) process used dry filtration technology to remove essentially all the fine particulates from the syngas, while the acid gas removal system (UOP's SelexolTM process) at the plant captured carbon dioxide from the syngas, diverting it for use in enhanced oil recovery (EOR) and making the Kemper facility's carbon emissions comparable to those of a similarly sized natural gas-fired combined cycle power plant. The facility's two Siemens SGT6-5000F gas turbines operated reliably on the high hydrogen, lignite-derived low Btu syngas from air-blown gasification operations. Kemper operations demonstrated excellent environmental performance, with emissions of various components well below the permit levels that were based on other IGCC plant performances and other national standards.

This paper discusses integrated plant operations and performance of the major components of the TRIGTM facility and compiles relevant experience and data gathered over the operation of the project. The paper also includes a selection of major lessons learned during various phases of the project from design through operations of the first-of-a-kind plant.

30.4 The Osaki CoolGen Oxygen-Blown IGCC with CO_2 Capture Demonstration Project

Yugo Ishizaki, OSAKI COOLGEN CORPORATION, JAPAN.

Coal will remain a primary fossil fuel, because of its wide distribution, abundant reserves, inexpensive and stable prices. Japan has extremely low energy self-sufficiency and coal power generation is positioned as an important power supply. However, the amount of carbon dioxide (CO2) emitted by coal utilization is larger than that of other fossil fuels. It is necessary that we find realistic solution to this problem for the world's sustainable development. Therefore, the Osaki CoolGen Project has been launched as a demonstration project aiming to achieve innovative low-carbon coal power generation that combines integrated coal gasification fuel cell combined cycle (IGFC) and CO_2 capture technology. This project consists of three steps. In the first step, highly-efficient oxygen-blown integrated coal gasification combined cycle (IGCC) was demonstrated. In the second step, the IGCC with CO_2 capture process will be verified. In the third step, a fuel cell unit is planned to be added to the IGCC in order to demonstrate an IGFC with CO_2 capture system.

Demonstration testing of the first step was conducted from March 2017 to October 2018. We have verified basic performance, controllability and operability. As a result, we have achieved world-class efficiency, environmental performance and operational flexibility. In particular, the load change rate has reached 16%/min and it greatly surpassed that of conventional pulverized coal fired power plant. Our IGCC having advanced flexibility contributes to the power grid stability while renewables are rapidly expanding.

In the second step, construction of CO_2 capture unit is now underway to start demonstration test from late 2019. We have adopted pre-combustion CO2 capture using physical solvent to reduce the energy loss of carbon capture. The third step commenced in March 2019.

In this presentation, operation summary of our IGCC plant and demonstration plan of IGCC with CO_2 capture will be introduced.

POSTER SESSIONS

GT: GASIFICATION TECHNOLOGIES

GT-P1 Bio-char and Ni-bio-char; a Sustainable Catalysts for Treatment of Tar from Co-gasification of Coal and Biomass in a Fluidised Bed Gasifier

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University of Johannesburg; M.O. Daramola, University of the Witwatersrand;
SOUTH AFRICA.

The production of tar during biomass gasification or co-gasification of biomass and coal causes a big setback in syngas production. Agglomeration and blockages of piping and valves of end-user facilities occurs due to polymerisation and condensation of tar. Catalysts are employed to crack tars hence; reducing its production and the cost of gas cleaning. The quality and yield of syngas are improved in the process. In this study, 3 biochar based (corn cob (CC-BC), sugarcane bagasse (SCB-BC), & pine sawdust (PSD-BC) and 3 Ni-biochar based catalysts (Ni-CC-BC), Ni-SCB-BC, & Ni-PSD-BC were used to carry out the tar treatment. The Ni-biochar based catalysts were synthesised via wet incipient impregnation method, and using Ni-to-Biochar ratio of 10:15. The tars that were treated were produced from Coal + CC, Coal + SCB, & Coal + PSD, and were referred to as CCC-T, CSCB-T, & CPSD-T, respectively. Averagely, the percentage amount of tar conversion (PTC) obtained from the optimum catalysts: PSD-BC and Ni-PSD-BC were around 89.76 and 96.73 %, respectively. At 900 OC and conversion times of 10, 15, & 20 min, the Ni-biochar catalysts were more efficient than that of biochar by 7.87, 3.87, & 3.79 %, respectively. Finally, a comprehensive tar treatment model was developed.

GT-P2 Ca/Na Compounds Catalyzed Coal Pyrolysis and Char Gasification with H_2O

Yonghui Bai, Guangsuo Yu, Xudong Song, Weiguang Su, Jiaofei Wang, Ningxia University, CHINA.

The main aim of this work is to investigate the effects of Ca/Na compounds on coal pyrolysis, gasification reactivity as well as char characteristics during gasification. The pyrolysis and gasification tests of different metal loaded coals were performed on thermo gravimetric analyzer and fixed bed reactor. The raw and gasified chars were prepared and characterized by nitrogen adsorption, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results indicate that Ca coexist with Na has a better catalytic activity compared to Ca and Na alone. The addition of metals can promote the pyrolysis gas release in advance and increase the release amount of H2 and CO_2. The present of Ca/Na compounds have no significant effect on pore structure evolution during pyrolysis, but it inhibits the aromatic structure condensation of the coal char. The addition of Na and Ca is beneficial to the formation of micropores and mesopores respectively during gasification, the simultaneous existence of Ca and Na results in a more abundant pore structure. Both Ca and Na can inhibit the condensation of aromatic structures during coal char gasification, Ca together with Na will make the char has a higher degree of disorder. The interaction between Ca and Na with coal char makes the carbon matrix easier to be attacked by H2O to form more active intermediates. Redox experiments further verified that more active intermediates were generated during the gasification of Ca/Na loaded char.

GT-P3 Study on Carbon Residue Formation Mechanism in Coal Gasification Slagging Process Based on Spectral Visualization Analysis

Xudong Song, Guangsuo Yu, Weiguang Su, Yonghui Bai, Jiaofei Wang, Doctor, Ningxia University, CHINA.

Entrained flow coal gasification technology is the key development direction of clean and efficient utilization of coal. Carbon residue generated in the process of slag formation of gasifier will affect the efficient operation of gasifier. By studying the formation mechanism of carbon residue in the process of slag formation and analyzing the process of carbon residue formation, theoretical support can be provided for the reduction of carbon residue content of slag in gasifier. Combined with spectral diagnosis and high temperature stage microscope technology, the mechanism of carbon residue formation during coal particle deposition in slag surface was studied. The results showed that, the reaction rate of coal on the slag surface increased clearly, which indicated that coal particle on the slag surface had a higher temperature. High temperature caused the slag flow and the unreacted carbon were encapsulated in slag, and Na and K in coal particles also promoted the slag generation.

GT-P4 An Experimental Study on High Temperature ESP Under Coal Pyrolysis Gas

Quanlin Chen, Jianmeng Cen, Mengxiang Fang, Qinhui Wang,
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High temperature dust removal technologies are very important to the development of clean coal utilization technologies, such as pressurized fluidized bed combustion (PFBC), integrated gasification combined cycle (IGCC) and coal poly-generation system. Electrostatic precipitator has the advantages of high dust removal efficiency and low pressure drop, thus, it is a promising technology in the field of high temperature dust removal. In order to understand the property of high-temperature ESP of coal pyrolysis gas, a lab scale electrostatic precipitator has been set up to study the influence of temperature and atmosphere on electrostatic precipitation. Under air gas medium, as the temperature increases from 400 °C to 600 °C, the maximum dust removal efficiency dropped from 99.65% to 96.01%, while the energy consumption index increased from 24.58 W/(g/Nm3) to 51.6 W/(g/Nm^3). Compared with air atmosphere, the maximum dust removal efficiency of coal pyrolysis gas is lower and energy consumption is higher. At 400 °C, the dust removal efficiency and energy consumption of air are 99.65% and 24.58 W/(g/Nm3), and those of coal pyrolysis gas are 90.52% and 49.35 W/(g/Nm3), respectively. In order to solve the problems of low efficiency and high energy consumption in electrostatic precipitation of high temperature coal pyrolysis gas, this work studied the influence of gas conditioning and positive power supply on the operation of ESP. At 400 °C, the maximum collection efficiency of ESP under coal pyrolysis gas media increases by 6.02% through gas conditioning. However, the improvement effect of gas conditioning on collection efficiency is weakened with the increase of temperature. At 600 °C, the maximum collection efficiency of ESP under coal pyrolysis gas media increases by 11.8% through positive power supply. As temperature increases, the improvement effect of positive power supply on collection efficiency increases. The results are beneficial to the design and application of high temperature ESP in the field of IGCC, PFBC, and coal poly-generation system.

GT-P5 Techno-Economic Analysis of Coal Dual-Bed Pyrolysis Polygeneration System Coupled with Pulverized Power Plant

Kaikun Li, Qinhui Wang, Chunjiang Yu, Mengxiang Fang, Zhongyang Luo,
Zhejiang University, CHINA.

China is well-known for its large coal reserve, especially for low-rank coals. With its high inherent water content, the transportation and combustion of low-rank coals is considerably uneconomical. Furthermore, to eliminate the serious environmental problems caused by coal-fired power plants, many efforts have been made to develop a clean coal utilization technology. A low-rank coal pyrolysis-based staged conversion technology co-producing tar, char and gas in dual fluidized beds is proposed. In aforementioned polygeneration system, coal was first pyrolyzed to produce char, tar and hot coal gas. The char generated in the fluidized pyrolyzer was partially combusted in the char heating furnace with air. The heated hot char was used as solid heat carriers for coal pyrolysis process. Based on the dual-bed coal pyrolysis process, two kinds of technical routes were proposed, (a) Tar was considered as final products, coal gas after cooled and cleaned was sent to synthesize SNG. Char was fired in a pulverized power plant for electricity; (b) Coal gas for SNG production, char for power generation, and tar was reacted with H2 which was separated from the clean syngas to synthesize crude light oil. Simulation of the two polygeneration plants was conducted using Aspen Plus. Two RYield modules were used to simulate the coal pyrolysis and char decomposition process, respectively. Partial combustion of char was modeled by the RGibbs module, based on the Gibbs free energy minimization method. Moreover, MHeatX module for heat recovery, Sep module for acid gas removal process, and REquil modules for SNG formation reactors. Several Turbine blocks were used to simulate different pressure cylinders for power generation. According to the results obtained from the simulation, thermodynamic and economic analysis were calculated and discussed. The total energy efficiency of plant (a) can reach 54.82%, which is 2.86% higher than that of plant (b). Accordingly, the exergy efficiency is 51.84% and 47.95%, respectively. Due to the investment of a tar hydrogenation unit, the total plant cost of (b) is a little higher than that of (a). However, the IRR (Internal Rate of Return) of (b) is 5.23% higher than that of (a), which is the contribution of the higher price of crude light oil. In conclusion, there are practical and economic advantages to establish dual-bed coal pyrolysis-based staged conversion polygeneration system coupled with pulverized power plant.

GT-P6 Isotopic Tracer Study of the Integrated Process of Coal Pyrolysis with Steam Reforming of Methanol

Xin-fu He, Jun Zhou, Xiao-qin Zhang, An-ning Zhou, Zhi-yuan Yang, Xi'an University of Science & Technology, CHINA.

Coal pyrolysis is one of the most important utilization technologies for low rank coal. However, the existing pyrolysis technologies have the problems of low tar yield and high content of heavy components in tar. Our previous research work shows that the integrated process of coal pyrolysis (CP) and steam reforming of methanol (SRM) can significantly improve tar yield and quality during pyrolysis. In order to explore the mechanism of the CP-SRM integrated process, we replaced the common methanol with CD3OD for the CP-SRM process. The hydrogen isotope composition in tar and char were analyzed on EA-IRMS, and the isotope content of different samples was compared by the value of R. The R value of hydrogen in representative monomer compounds such as 1-methylnaphthalene and 2-cresol in tar were analyzed on GC-Py-IRMS. The results show that the R value of hydrogen in the tar, char and monomer compounds of tar, during the isotope tracer IPCPSRMD (Z205) are much higher than the R value in the products obtained by pyrolysis under N2 atmosphere. It is indicated that during CP-SRM integrated process, H-D and D-radicals participated in the coal pyrolysis process and entered the compounds like 2-cresol,2- methyl naphthalene and alkane compounds in the tar. The free radicals generated by the CP-SRM process stabilized the macromolecular fragments produced by coal pyrolysis and inhibit the polycondensation between coal macromolecules. Therefore, the purpose of improving tar yield and quality was achieved.

CCD: CLEAN COAL DEMONSTRATION AND COMMERCIAL PROJECTS

CCD-1 High Yield and Economical Production of Rare Earth Elements from Coal Ash

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Coal and coal byproducts are a potential source of REEs, particularly HREEs. Demonstration of technologies to recover REYSc from these feedstocks will enable utilization of coal mining/coal combustion waste product in environmentally benign ways to produce REEs of strategic importance for the United States while generating jobs and economic growth in economically-depressed regions of this country. Under sponsorship from the Department of Energy, the team of Physical Sciences Inc., University of Kentucky/Center for Applied Energy Research, and Winner Water Services is developing and demonstrating a pilot scale plant to economically produce salable REE-rich concentrates including yttrium and scandium (REYSc) and commercially viable co-products from coal ash feedstock using environmentally safe and high-yield physical and chemical enrichment/recovery processes. The pilot plant will operate at the scale of approximately 0.4-1 tons per day (tpd) ash throughput for physical processing and about 0.5 tpd for chemical processing, producing at least 50 g of dry REYSc nitrates concentrate containing more than 10 percent by weight of REYSc, and targeting 500 g of dry REYSc nitrates concentrate containing more than 20 percent REYSc by weight. The ash feedstock contains at least 500 ppm of REYSc content. The data obtained from the pilot plant operations will be used to enhance and validate the techno-economic analysis that was completed for both the physical and chemical processing plants at a scale of 600 tpd, and use it to design a commercial scale plant (hundreds of tpd throughput) with return on investment in less than seven years. This paper will describe the approach and the key results with regard to process optimization, scale up and pilot plant implementation. The paper will provide a comprehensive overview of the overall process that provides economical production of REY concentrates applications. The production of valuable coproducts will also be discussed. Development and demonstration of modular, transportable pilot scale physical and chemical plants for REYSc recovery from coal ash, including enhancement and validation of a techno-economic model of a pilot plant operations data, will enable the design of a commercial scale (hundreds of tpd) REYSc plant.

CT: COMBUSTION TECHNOLOGIES

CT-P1 Physicochemical Characteristics of Fine Particles Collected from WESP in a Coal-Fired Power Plant

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Particulate matter collected from ESP (electrostatic precipitator) and WESP (wet electrostatic precipitator) of a demonstration ultra-low emission coal-fired power plant in China were systematically collected and well characterized. X-ray diffraction (XRD), X-ray fluorescence (XRF), specific surface area test (BET), Scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and Laser particle size analyzer were adopted for the characterization for understanding the physicochemical characteristics of fine particles from the typical ultra-low emission coal-fired power plant.

The results indicated that particle size of the fly ash from ESP is decreasing from the No.1 electric fields to No.5. Particles in No.1 electric fields are in size of 10-100 μm, while particles in other electric fields are in the size of 1-10μm. A small quantity of large particles with size of 300-1000μm can be identified in the ashes from ESP. The surface area of the fly ashes from No.1 to No.5 electric field increases from 1.5 mg2/g to 3.23 mg2/g. Alumina-silicates are the dominate phase mineral compositions in the fly ashes from ESP, and a certain amount of Ca and S are also found in the fly ashes. All the particles present as isolated fine particles without any agglomeration. The amount of fine particles from WESP are extremely small. The physicochemical characteristics are distinct from that in ESP. It can be identified that some alkali metal contained minerals are found in the fly ash besides alumina silicate. Meanwhile, Ca and S content obviously decrease in comparison to that in the fly ash from ESP. Further, most particles are in size of 50nm -500nm, which is obviously smaller than that in ESP. However, a large fraction of the particles agglomerated together. The phenomena of agglomeration not only exist between the large particles and fine particles, but also exists between fine particles and fine particles. The obvious agglomeration phenomena indicate that ultra-fine particles would get together and grow up to larger particles, which would be much easier to be removed by the WESP.

CT-P2 Modification of Red Mud for the Removal of Mercury from Coal Combustion Flue Gases

Muhammad Sarfraz, Yang Li, Lixin Dang, Haoquan Hu,
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This study seeks to remove mercury (Hg0) from the coal combustion flue gases, through red mud, a solid waste residue derived from the production of alumina, modified by hydrogen halide impregnation. X-ray diffraction, X-ray fluorescence, X-ray photoelectron spectroscopy, scanning electron microscopy and Brunauer-Emmett-Teller were used to characterize these materials physically and chemically. In order to study the effects of some major parameters such as loading amount, reaction temperature and main flue gas components on Hg0 removal, a number of experiments were conducted. Furthermore, the reaction mechanism and kinetic model analyses of Hg0 removal were examined. The results show that the modification of red mud by hydrogen halide considerably improves the Hg0 removal performance. Hg0 removal efficiency increases with increasing the reaction temperature, loading amount, O2 concentration and NO concentration. The increase of SO2 concentration decreases the Hg0 capture. The process of Hg0 adsorption on modified red mud conforms to the pseudo-second order kinetic model.

CT-P3 Copper Iron Oxide Modification Magnetosphere Catalyst from Fly Ash for Mercury Oxidation in Flue Gases

Yang Li, Lixin Dang, He Yang, Lijun Jin, Haoquan Hu,
Dalian University of Technology, CHINA.

In this paper, magnetic catalysts $CuO{\cdot}Fe_2O_3$/MF were prepared by modified sol-gel and pyrolysis methods. The effects of simulated flue gas, temperature and catalyst suitability was studied on a fixed bed reaction system. PPMS-VSM, XRD, BET, TG, SEM-EDX and XPS were involved to characterize the catalysts. The results show that the catalysts have superior Hg^0 oxidative activity and stability in the temperature range of 100-350 °C; The catalysts contains a large number of oxygen; Cu was the major active site on the catalyst surface; Fe in the catalyst can be used to resist sulfur; so the catalyst have a wide applicability on complex condition. The effect of simulated flue gas composition was also analyzed. It is showed that CO_2 could enhance stability of the catalyst; HCl promotes Hg^0 oxidation; results of the influence of NO and SO_2 were uncertain, due to the differences in concentration and reaction temperature of simulated flue gas. The optimum loading weight of CuO and Fe_2O_3 on catalysts can be adjusted due to temperature and composition of coal combustion flue gas. The catalyst continuously reacted in different simulated atmospheres for 10h, with a Hg^0 oxidation activity of 90%. The magnetism of the catalysts is significantly higher than the magnetospheres collected from fly ash; the mercury oxidative reaction almost has no affectation on the magnetism of $CuO{\cdot}Fe_2O_3$/MF. Therefore, the catalyst can be a promising material for Hg removal and relatively easy to separate and recycle before the following utilization of fly ash.

GF: CLEAN COAL AND GAS TO FUELS

GF-P1 Influence of Preparation Method on Structure of Ni2P/SiO2 Catalyst and its Hydrogenation Performance of Naphthalene Over

Zhi-Fen Yang, Jie-Ying Jing, Dao-Chen Liu, Jiu-Zhan Wang, Zhi-Qang Qie, Jie Feng,
Wen-Ying Li, Taiyuan University of Technology, CHINA.

The cycloalkanes derived from saturated hydrogenation of polycyclic aromatic hydrocarbons are ideal components for high-performance aviation jet fuel. In this work, naphthalene hydrogenation to decalin was investigated over Ni_2P/SiO_2 catalysts. The Ni_2P/SiO_2 catalysts were prepared by temperature-programed method and decomposition of hypophosphite method, respectively. It is found that the Ni_2P/SiO_2 prepared by temperature-programed method showed higher selectivity for decalin at the first two hours of reaction, then the selectivity for decalin was decreased to a stable value. However, the Ni_2P/SiO_2 prepared by decomposition of hypophosphite method showed lower selectivity for decalin. The hydrogenation performance of Ni2P/SiO2 catalysts prepared by different method was closely related to the interaction between active components and supports, crystallite size and the composition of the active components.

CM: CARBON MANAGEMENT

CM-P1 Levelized Cost of CO_2 Captured Using Different Physical Solvents in Precombustion Applications

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Aspen Plus v8.8 was used to simulate a CO_2 capture process from a typical fuel gas stream in a 543-MW precombustion plant using four different physical solvents (Selexol, methanol, NMP, and [hmim][Tf2N]) in a countercurrent high-pressure packed-bed absorber under a wide range of operating temperatures. Selexol is dimethylether of polyethylene glycol, NMP is n-methyl-2-pyrrolidone, and [hmim][Tf2N] is an ionic liquid (IL) 1-hexyl-3-methyl-imidazolium bis(trifluoro-methylsulfonyl) amide. Three pressure-swing flash drums were also used in the process for solvent regeneration. The constraints implemented in the process simulation were (1) minimum 90% CO_2 capture, (2) no flooding in the absorber, (2) minimum irrigated pressure loss, (3) minimum water concentration (< 600 ppm) in the CO_2 stream sent for sequestration and (4) minimum loss (< 0.5 mol%) of fuel gases (H_2, CO, CH_4) with the CO_2 steam sent for sequestration. Due to the huge process fuel gas flow rate (155 kg/s), the absorber inside diameter and packed-height were varied from 6 to 8 m and from the 36 to 48 m, respectively. Two different packings, Mellapak 250Y (specific surface area = 256 m^{-1} and voidage = 96%) and IMTP50 (specific surface area = 102 m^{-1} and voidage = 98%), were used in the simulation. The process pressure was maintained around 51 bar and the operating temperatures for Selexol, NMP and [hmim][Tf2N] ranged from 0 to 50 ºC, whereas those of methanol were varied from - 50 to 0 ºC.

The physicochemical properties of the solvents were collected from the literature and the solubilities of the various fuel gas constituents in each solvent were modeled using the Perturbed Chain Statistical Association Fluid Theory (PC-SAFT) Equation-of-State (EOS), which was ultimately implemented in Aspen Plus. The levelized cost of CO_2 captured (LCOC), expressed in USD/ton of CO_2 captured, was calculated and used to determine the economic feasibility of the precombustion process under given conditions. The Aspen Plus simulation results indicated that for the four physical solvents used, the CO_2 capture process using the structured packing (Mellapak 250Y) had a lower LCOC under all simulated conditions when compared with that using the random packing (IMTP50), which might be related to the higher specific surface area of the former. The CO_2 capture process carried out at low temperatures showed lower LCOC than that at high temperature due to the high solubility of CO_2 in the solvents at low temperatures. Comparing the lowest LCOC values for the four solvents used, Selexol showed ($11.30) at 5 ºC and 10 ºC, NMP showed ($21.70) at 0 ºC; methanol showed ($15.6) at - 50 ºC; and [hmim][Tf2N] showed ($20.96) at 0 ºC. In this simulation, the cost per liter of Selexol, NMP, methanol and [hmim][Tf2N] was $4.00, $2.00, $0.57 and $415, respectively. Therefore, due to its thermal and chemical stabilities, [hmim][Tf2N] would have great potential for CO_2 capture in precombustion applications, if its cost is reduced.

CM-P2 Modeling of CO_2 Absorption from Gas Mixtures Using Chemical Absorbents in Adiabatic Packed-Beds

Rui Wang, Husain Ashkanani, University of Pittsburgh; Bingyun Li, West Virginia University; Badie Morsi, University of Pittsburgh; USA.

A five-components mathematical model for CO_2 absorption from gaseous mixtures by aqueous solutions of two chemical absorbents, AMP (2-amino-2-methyl-1-propanol, $C_4H_{11}NO$) and sodium glycinate (Na Gly, $C_2H_4NNaO_2$), in small-scale (0.1 m ID) and large-scale (1.5 m ID) countercurrent adiabatic packed-bed absorbers was developed. The material and energy balance equations were derived for the gas and liquid phases, similar to Pandya's approach (1983) and an extensive literature search was conducted to obtain, correlate and compile the required equation parameters, including the physico-chemical and thermodynamic properties, reaction rate kinetics, gas-liquid mass transfer coefficients, and the hydrodynamic as well as flooding criteria. The model was implemented in MATLAB 2017b to solve the combined material and energy balances under different boundary conditions and packing types and to predict the profiles along the absorber height of the CO_2 absorption efficiency, CO_2 loading, CO_2 mole fraction, gas and liquid phase temperatures, in addition to the enhancement factor and Hatta number to assess the speed of the chemical reactions taking place.

The model predictions were first validated using four different runs of the experimental data by Tontiwachwuthikul et al. (1992) obtained in a small-scale absorber (0.1 m ID) for CO_2 absorption from a CO_2-air mixture using AMP aqueous solutions. Generally, the model predictions were in good agreement with the experimental data for CO_2 loading and liquid temperature, however, there was a slight deviation in the predicted CO_2 mole fraction profiles, which were attributed to the experimental errors in the CO_2 material balance reported by Tontiwachwuthikul et al. (1992).

The validated model was used to predict the behavior of a countercurrent adiabatic small-scale (0.1 m ID) packed-bed absorber with (13 mm ceramic Berl Saddle) for CO_2 capture from a CO_2-air gaseous mixture using SG aqueous solutions under identical inlet operating conditions to those of AMP. A direct comparison between CO_2 absorption efficiencies by the two absorbents showed that AMP has a higher CO_2 absorption efficiency and CO_2 loading than those of SG due to the former's greater reaction rate constant (k_2) under similar operating conditions.

CM-P3 Postcombustion CO_2 Capture in a Countercurrent Packed-bed Absorbers using Monoethanolamine Aqueous Solutions

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Carbon capture and sequestration (CCS) entails carbon dioxide (CO2) capture from different point sources, such as coal-powered plants and/or Integrate Gasification Combined Cycle (IGCC), then the concentrated captured CO2 is compressed and sent to sequestration sites, including depleted oil and/or gas reservoirs, deep saline water aquifers, deep unminable coal seams, or in ocean deep in the form of CO2 hydrates. This study is focusing on CO2 capture from the flue gas produced from coal-powered plants, known as postcombustion capture, using Monoethanolamine (MEA) aqueous solutions in a countercurrent adiabatic packed-bed absorber operating under ambient conditions. A comprehensive mathematical model was developed in Matlab (2016a) to predict the behavior of a pilot-plant packed-bed absorber. The model is based on rigorous procedure for adiabatic gas absorption with second-order chemical reaction by Pandya [1]. Five components, CO2, air, MEA, H2O and carbamates, were considered in the material and energy balances derived in the absorber. The required model equation parameters including, reaction kinetics of CO2 with aqueous MEA solution, physicochemical properties of the five components, mass and heat transfer coefficients were collected from the literature and included in this model.

The model predictions were validated using the experimental results obtained from a pilot plant study with random packing by Tontiwachwuthikul et al. [2]. Their pilot-plant is 0.1 m internal diameter (ID), 6.55 m height packed with 12.7 mm Berl Saddles and it was used for CO2 capture from a mixture in air with MEA. The comparisons between model predictions and experimental data for CO2 mole fraction profile, MEA concentration profile, and liquid-phase temperature profile were satisfactory, except at high CO2 loading. The rate-based MEA model in Aspen Plus software is currently being used to provide another validation of the Matlab model predictions.

[1] J. D. Pandya, "Adiabatic Gas Absorption And Stripping With Chemical Reaction In Packed Towers," Chemical Engineering Communications, Vol. 19, pp. 343-361, 1983.

[2] P. Tontiwachwuthikul, A. Meisen, And C. J. Lim, "CO2 Absorption By NaOH , Monoethanolamine 2-Amino-2-Methyl-1-Propanol Solutions In A Packed Column," Chemical Engineering Science, Vol. 47, No. 2, pp. 381-390, 1992.

CM-P4 The Influence of Aqueous H_2O_2 Oxidation of Columnar Activated Carbon (CAC) on Photocatalytic Performance of $Ti_1/Li_3/Al_2$-LDHs- CAC Composites in Reduction of CO_2 with Water

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The Photo-catalytic CO2 reduction is very difficult, that is mainly owing to the difficulty of achieving effective adsorption and activation of CO2 molecules. We have found that Ti1/Li3/Al2-LDHs/ columnar activated carbon (CAC) composites is a kind of bi-functional photo-catalyst which can effective adsorb CO2 and also photo-catalytically reduce CO2 with H2O to CO and CH4 under UV irradiation, but the conversion yields can only reach 27.51μmol/g-cat and 1.12μmol/g-cat respectively. The main reason is that the surface of CAC has less oxygen containing functional groups, which result in Ti1/Li3/Al2-LDHs serious agglomeration. In this paper, the surface of the CAC was firstly modified by aqueous H2O2 oxidation. The effect of aqueous H2O2 concentration on photo-catalytic performance of Ti1/Li3/Al2-LDHs/CAC composite was further studied. The results showed that aqueous H2O2 concentrations have a great effect on photo-catalytic performance of Ti1/Li3/Al2-LDHs/oxidized CAC. The photo-catalytically reduction products CO2 with H2O is mainly CO over Ti1/Li3/Al2-LDHs/oxidized CAC under UV irradiation. When aqueous H2O2 concentration was increased from 3% to 9%, the CO yield increased from 23.42μmol/g-cat to 61.08μmol/gcat. The CO yield is higher over Ti1/Li3/Al2-LDHs/oxidized CAC at 9% aqueous H2O2 than Ti1/Li3/Al2-LDHs/CAC. Aqueous H2O2 modification of OAC can effectively enhance the photo-catalytic performance for reduction of CO2 with H2O.

CM-P5 Computational Modelling of Bulk ZIF-8 for Carbon Capture Applications

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Zeolite imidazolate frameworks (ZIFs) have selective adsorption properties and are useful materials for gas separation. When compared to traditional chemical sorbents (mostly amines), ZIFs have (1) high CO_2 loading capacity, (2) lower-energy consumption, (3) high thermal and chemical stability, (4) fewer mechanical requirements and lower corrosion rates (Banerjee et al, Science 2008, **319**, 939; Park et al, Proc. Natl. Acad. Sci. U.S.A. 2006, **103**, 10186, Nordin, et al **RSC Adv.**, 2014,**4**, 52530-52541). Several theoretical and experimental studies reveal that due to its hybrid metal/linker type structure, ZIF-8 material is highly responsive to changes of the external physical and chemical environments. Interaction of sorbent materials with gas molecules plays a significant role in identifying materials' nature of selective adsorption and diffusion for some gas molecules over others. Therefore, understanding of ZIF-8 interaction with different gas molecules is crucial for further experimental and theoretical studies while considering the bulk, surface and interface composite model designs. Computational studies based on the density functional theory (DFT) can capture the fundamental properties of interactions and gas diffusion mechanisms that can be directly correlated with the experimental observations. Here we present our studies based on DFT calculations on CO_2 and CH_4 gas adsorption and diffusion in the bulk of ZIF-8. We evaluate the structural and electronic properties of bulk ZIF-8, determine the strong adsorption sites for gas molecules, and calculate the diffusion barriers for CO_2 and CH_4. Our calculations include long-range dispersion interactions. We analyze adsorption properties by fixing as well as relaxing both the framework atoms and gas molecules, examine their effects on gas diffusion properties, and compare with the experimental results where available. We find that the CO_2 and CH_4 adsorption energies at the strongest adsorption sites are 5.01 and 4.65 kcal/mol, respectively. The diffusion energy barriers for CO_2 and CH_4 are attractive, and are calculated to be -3.65 and -4.01 kcal/mol, respectively. With the above value of diffusion barrier, the diffusion coefficient for CO_2 is calculated to be 1×10^{-10} m^2/s.

CS: COAL SCIENCE

CS-P1 Low Rank Coal Upgrading and Separation Method and Slime Reduction Process Based on the Flip-Flow Screen Classification and Shallow Tank Heavy Medium Separator

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Coal is the main source of energy in China and contributes to the national economy. However, the use of coal is accompanied by environmental problems. For low rank coal preparation plant, with the aim of mitigating the technical difficulties encountered in the full-size separation and upgrading of power coal, a novel and low cost separation process is proposed here. To this cleaner production and technical processes, the characteristics of both a 3 mm flip-flow screen and a dense-medium separator were thoroughly investigated. This paper aims at resolving the difficulty of upgrading the clay-based coal in China. A retreating sieve 6/3 mm dry depth screening along with the classification of heavy-medium washing process was proposed. For the 3 mm flip-flow screen, the response of the working frequency and tension to the movement and screening characteristics was investigated. The screening efficiency was found to reach as high as 81.77%, and the undersize fraction was reduced to only 2% under reasonable control of parameters. A multi-parameter control method (based upon location, flow rate and feed quantity) is put forward for the separation of heavy-medium and heavy-medium in shallow tank. When the relative height of the feeding position was 70% and the flow rate was 75%, the coal separation was the best. The high separation efficiency of 100-3mm wide grain grade coal has also been realized. The yield of clear coal was 83.72%, and the value of E was 0.055 g/cm 3. The cleaning process can optimize the upgrading and utilization process of clay-based coal efficiently and provide a new technological process for separation.

CS-P2 Effects of Different Acids on Solvent Extraction of REEs from Coal Ash

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Coal ash is a combustion residual produced from coal-fired power plants. In 2017, 111.3 million tons of coal ash were produced in the United States, out of which 64 percent was recycled and beneficially reused in concrete, cement, structural fills, road base, soil modification, wallboard, agriculture, etc. (American Coal Ash Association). Another possible beneficial use of coal ash is to recover rare earth elements (REEs) from the ash, which contains around 300 ppm of REEs. REEs are critical elements in high-tech devices, cars, clean energy, and defense. Since the REE supply is highly dependent on other countries, the U.S. is currently seeking alternative methods of domestic REE production, and abundant coal ash could be a potential resource for a reliable supply of REEs in the U.S.

In order to extract REEs from coal ash, the ash first needs to be dissolved in acid to generate REEs-bearing leachate. Afterward, solvent extraction takes place to separate out REEs from the leachate. Extractants play a critical role in solvent extraction to separate REEs from the leachate, and their extractabilities are affected by different acidic environments. Therefore, efforts on the optimization of organic phase consisting of extractant and diluent with different kinds of acid leachate will be discussed in this presentation. The optimized REE extraction conditions will be applied into a membrane solvent extraction system for scale-up design in future work.

CMN: COAL MINING, PREPARATION, AND HANDLING

CMN-P1 In-Situ Testing and Data Applications for Upstream-Constructed Coal Refuse Impoundments

Abeera Batool, Blaise Genes, GAI Consultants, Inc, USA.

Upstream-Constructed Coal Refuse Impoundments have unique characteristics as compared to the other engineering structures as the hydraulically-deposited fine coal refuse (FCR) is used as the foundation material. This paper outlines the key design aspects for such structures including developing and implementing risk-appropriate in-situ field and laboratory testing, characterizing embankment and foundation materials, and most significantly, characterizing of the FCR material. FCR in particular requires comprehensive evaluation of the physical properties, undrained shear strength, as well as seepage and settlement parameters. These parameters are then used to analyze the stability during construction and determine the rate of placement/loading Coarse Coal Refuse (CCR) material can take place on top of the FCR without compromising the stability of the system. The maximum loading rate is the rate at which the strength gained during the construction time period is greater than the strength required to achieve a factor of safety of 1.3 or greater. Generally, a safety factor of 1.3 is considered appropriate for such analysis, as it is treated as a short-term construction condition.

This paper provides information about developing the site exploration program for upstream-constructed coal refuse impoundments, and key elements required to obtain necessary information for site characterization. The focus of the paper is on cone penetration testing (CPT), and CPT data variations for different materials (depending on their behavior) are discussed. The details are also provided for the use of seismic CPT with pore pressure measurement (SCPTu) for upstream construction, especially pore pressure dissipations tests. The pore pressure dissipation data obtained from SCPTu can be interpreted to obtain the estimates of groundwater conditions, and seepage properties of the materials, particularly permeability and consolidation characteristics. The paper outlines how this information obtained from the CPT data can be incorporated into the analyses.

A case study is presented in which the required strength of the FCR is determined using the stability analysis to achieve the short-term factor of safety of 1.3. This strength is then compared with the strength that is gained by the FCR material for different construction/loading rates. Once the loading rate is established, and placement of the fill starts, the next step is monitoring the response of the FCR material to ensure that it is consistent with the assumptions made in the analyses. This is achieved by installing rapid response piezometers at strategic locations and monitoring the excess pore pressures developed during construction. Action levels are developed for monitoring of the piezometers, which indicate that the system will remain stable (having factor of safety of 1.3 or greater) as long as the excess pore pressure readings from installed piezometers are below the action levels. The monitoring of the pore pressures from the same case study as discussed above will also be presented and will be compared to the action levels.

In conclusion, this paper presents the details of upstream-constructed coal refuse impoundments, developing the investigation plan for site characterization for such impoundments including effective use of SCPTu data for loading rate analyses, and effective monitoring of the performance of the system.

CB: COAL BED METHANE AND SHALE GAS

CB-P1 Macromolecular Model of Shenmu Coal and Its Molecular Mechanism of Methane Adsorption

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The chemical structure of coal has special complexity, diversity and heterogeneity, and its structural model must be established for specific coal samples. As a new type of clean energy, coalbed methane is mainly in the coalbed bed in the adsorption state. Therefore, it is very important to study the interaction between methane molecules and coal macromolecules for the exploitation of coalbed methane.

Using equipment such as Fourier transform infrared spectroscopy (FTIR), 13C solid-state nuclear magnetic resonance (13C NMR), X-ray diffractometry (XRD), and high-resolution transmission electron microscopy (HETEM), combined with the results of elemental analysis and industrial analysis, the macromolecular structure model of the Buertai coal sample from Shenmu coal mine area was constructed. The interaction mechanism between coal macromolecules and methane was studied by Materials studio 8.0 (MS). The results show that temperature and pressure have a great influence on the adsorption of methane by coal molecules. With the increase of temperature, the adsorption amount of methane is smaller, while with the increase of pressure, the adsorption amount of methane increases, and finally approaches a critical value. In the environmental temperature of 303 K and 3 MPa ambient pressure, the relative error of Langmuir adsorption constant (a) in simulated and experimental isotherm adsorption results is 9.7%, indicating that it is feasible to study the adsorption behavior of methane gas by constructing coal macromolecules. In saturated adsorption, the saturated adsorption capacity of coal macromolecular structure for methane molecules is 10, and the adsorption energy of a single methane molecule is -2.45 kcal/mol. Among the effects of functional groups on methane adsorption, carbonyl has the greatest influence on the adsorption of methane.

CB-P2 The Ultra-low Concentration Coal-bed Methane Fluidized Bed Oxidized Combustion System and Its Technical and Economic Evaluation Under Carbon Trading Mechanism

Zhongqing Yang, Xiuquan Li, Li Zhang, Lin Ding, Yunfei Yan, Chongqing University, CHINA.

The ultra-low concentration coal-bed methane (UCCM) is the coal-bed methane in which methane concentration is lower than 5%. UCCM always exits in waste coal mine and ventilation air. However, its low calorific value makes it difficult to use, and therefore, most untreated low-concentration methane is simply released to the atmosphere. The emission of UCCM causes the energy waste of non-renewable resources as well as the intensified greenhouse gas effects. The global warming potential of methane which is the main components of UCCM is 21 times larger than CO2. Therefore, it's essential to utilize UCCM in reasonable means. However, it is difficult to utilize this low-concentration methane by employing conventional combustion technology. Hence, an attractive alternative for this purpose is fluidized bed combustion, which involves complete oxidation at low temperature.

A fluidized bed combustion system which is suitable for burning ultra-low concentration coal-bed methane was introduced. The minimum concentration of system to maintain operation was analyzed. The effects of exhaust gas temperature and methane concentration to surplus heat were discussed. Techno-economics analyses were taken in the case of a coal mine in China. This project reduces CO_2 emissions. Selling the CO2 emission reduction in the international market brings additional income for the project and makes the project market competitive. The Net Present Value (NPV) analysis and Internal Rate Return (IRR) of this project were accounted for. To evaluate the capability of project to resist risk, break-even relationships between fixed cost, operating cost, income and production were analyzed. In addition, the sensitivity analysis of the four factors of sell price, operating cost, production and construction investment to the IRR was analyzed.

The results showed that the minimum concentration was increased linearly as the exhaust gas temperature increasing. The concentration of UCCM has significant effect on surplus heat of system. That is the surplus heat increased linearly with the addition of concentration. The lower exhaust temperature, the more surplus heat could be got at the same concentration. Similarly, the higher methane concentration, the more surplus heat could be got at the same exhaust temperature. Net Present Value and Internal Rate Return analysis indicate that the fluidized bed combustion system was feasible and environmental benefits could be got. Break-even Analysis and sensitivity analysis show that the project is feasible and has a good capacity to resist risk. It's cost-effective with implement of Clean Development Mechanism (CDM).

PP: POWER PLANTS

PP-P1 Situation and Discuss on Biomass Co-Combustion Technology for Power Generation in China

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The requirements of carbon reduction have been enhanced in recent years in China. Biomass co-combustion with coal for power generation could respond to China's energy transforming policy. The co-combustion technology can be divided into two different ways: direct and indirect co-combustion technology.

This paper reviewed the development of biomass co-combustion technology in China in recent years. The direct co-combustion technology could be built with less equipment and reduce the investment cost; Furthermore, the operation of the system is much easier than the indirect methods. However, the direct co-combustion technology is hard to monitor the amount of electricity generated by biomass, and thereby hard to obtain the policy allowances (or credits). Besides, some pollutant elements such as Na, K, Cl are rich in some biomass, which may enter into the coal fired boiler and lead to increased slagging, coking or corrosion.

The indirect co-combustion technology gasifies biomass first, and then sends syngas into the coal-fired boiler for power generation. This method could improve adaptability for different biomass, avoid coking and slagging and easy to calculate the electricity output power. On the other hand, the indirect way needs to use more equipment and require more investment capitals. Besides, the operation of a biomass gasifier is quite different from that of a coal-fired boiler and brings difficulties and challenges to operating staff. These problems are the reasons that the indirect co-combust technology is still not used widely in China.

Biomass co-combustion technology has been applied in several projects in China. Some technology problems could be resolved by improving the equipment and optimizing the operation parameters. The economics and current policies are the main factors that have limited the promotion of biomass co-combust technology in China.

PP-P2 Economical Study on a 10MW Scale Biomass Indirect Co-Combustion with Coal for Power Generation

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Biomass indirect co-combust with coal for power generation is one of the feasible ways in China's energy policy in recent years. This technology could use high parameter units in coal-fired power plants, and thereby has a higher efficiency. Indirect co-combustion technology turns biomass into syngas in a gasifier first, then the syngas is sent into the boiler and combust with coal for power generation. Compared with the direct co-combustion technology, indirect co-combustion technology could avoid the pollutants entered into the boilers and have little changes for the coal-fired boilers. Besides, the indirect co-combustion technology could easily monitor the volume, component and temperature of the syngas, and easier to get policy allowances (or credits). However, due to the allowances and the raw material cost having not been clear in different area of China, this technology could not be promoted widely in China.

This study analyzed the economics of a 10MW scale fluidized bed biomass gasifier. Raw material costs, product price, and policy allowances were considered in this paper. The results show that the raw material costs and policy allowances could affect the profits obviously. Biomass co-combustion project could have a better benefit when biomass electricity price is 0.75Yuan/kwh. It is hard to profit without any allowances when the raw material cost is higher than 350 Yuan/tonne. Due to the high value of biochar and tar, the multi-generation mode would have higher benefit. Considering the raw material cost and labor cost have been risen in China in recent years, the profit of biomass power generation is reduced remarkably. Multi-generation mode would increase the benefit of the project and should be promoted more widely.

REE: RARE EARTH ELEMENTS (REE) IN FOSSIL FUEL DERIVED SOLIDS AND LIQUIDS

REE-P1 Rare-Earth Elements (REEs) in U.S. Coal-Based Resources: Sampling, Characterization, and Round-Robin Interlaboratory Study

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The University of North Dakota Energy & Environmental Research Center (UND EERC) and the University of Kentucky, under contract with the U.S. Department of Energy National Energy Technology Laboratory, assessed rare-earth element (REE) concentrations in primarily western U.S. (85%) but also eastern U.S. (15%) coal and coal-related materials and conducted a round-robin interlaboratory analysis of selected samples for REEs. The REEs consist of the lanthanide series of elements with atomic numbers from 57–71 and also include yttrium and scandium. The project produced new data on the abundance and modes of occurrence of REEs in western U.S. coal resources from the Williston Basin (80% of western effort in North Dakota and Montana) and selected HREE (heavy REE) concentrations in resources from the Powder River Basin, San Juan Basin, Gulf Coast, and Central Appalachian Basin. The results of the sampling effort, which included over 500 samples, will be presented along with the round-robin interlaboratory study.

REE-P2 Rare Earth Element Occurrence and Distribution in Powder River Basin Coal Core, Wyoming

Davin Bagdonas, Charles Nye, University of Wyoming; Randal B. Thomas, LRST (Battelle), National Energy Technology Laboratory; Kelly K. Rose, National Energy Technology Laboratory; USA.

Trace element concentrations have been a focus of coal research for decades. A broader recognition of coal as an alternative resource for critical metals has led to a surge in interest understanding the distribution and occurrence of critical metals potential in US coals. Review of the USGS's COALQUAL database, in-house coal databases, and previous research on fly ashes by the U.S. Department of Energy (DOE) and the University of Wyoming Center for Economic Geology Research (CEGR) has identified certain coals that contain concentrations of rare earth elements (REE) above U.S. mean values that may represent ore targets for critical minerals. Evaluation of coal fired power station waste streams (fly ash and bottom ash), in comparison to USGS data sets, has identified Wyoming's Powder River Basin (PRB) as one area to focus for REE research. However, in terms of trace element chemistry and distribution, the PRB has remained one of the world's least well-understood major coal basins despite exhibiting potential REE enrichment. Persistent lack of publicly available trace element data for the PRB is surprising since the PRB encompasses the largest U.S. coal stock in terms of power station fuel use and coal reserves. Here, we evaluate a PRB coal core at high resolution for major and trace element concentrations including REE to identify locations of enrichment within a PRB coal. We identify locations that contain the highest REE values as well as make inferences about the geological and geochemical processes that may underlie these enrichment horizons. With potential REE enrichment mechanisms in mind, we also describe the utility of possible investigations of proxy major and trace elemental analyses to identifying REE enriched portions of PRB coals without requiring full REE digestions and analysis by ICP-MS. Within the coal core evaluated in this study two distinct types of REE relative enrichments can be described. We describe both volcanogenic and humic REE associations. Moreover, total concentrations of REE are highly variable with depth of the coal seam. Both total REE and individual REE species change in relative abundance indicating geochemical sorting. For example, total REE concentration varies from 100.1 to 1572.1 ppm, while in the same sample set critical REE (Nd, Eu, Tb, Dy, Er, and Y) range from 26.1 to 647.7 ppm and the percent of critical REEs ranges from 18.74% to 71.15%. Interlaboratory comparative assessment and data selection has also been conducted to verify these results and improve interpretation.

REE-P3 Rare and Rare Earth Elements in the Technogeneous Waste of Thermal Power Enterprises in Primorsky Krai of the Russian Federation and Methods of Effective Reclamation

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Rare and rare earth metals are strategic resources that play a key role for a number of sectors, such as IT, mobile, fuel and power, medical, automobile, and other sectors of the industrial production.

Studies on the composition of ash and slag waste at thermal power enterprises are widely represented in works of both foreign and domestic researchers. The content of rare and rare earth metals varies with regard to characteristics of the initial solid fuel and methods of its burning; however, it is noted that the majority of them are concentrated in the waste of heat power industry in the amount sufficient for the industrial reclamation. This said, even though the cost of reclamation is significantly lower (by 50-60%), reclamation itself requires more complex technological solutions due to specifics of ash and slag waste composition that has way more mineral forms than regular ores.

The collective of authors of this scientific work conducted the research on estimation of the content of rare and rare earth elements in the technogeneous waste of thermal power enterprises in Primorsky Krai of the Russian Federation. The ash and slag waste of CHPP, and Primorskaya GRES and CHPP-2, Vladivostok was selected as the research target. The following two fractions were reclaimed during the beneficiation process (flotation, magnet separation): the light non-magnetic and the heavy non-magnetic.

As shown through analysis (mass-spectrometry with inductively coupled plasma), the following rare and rare earth elements prevail in the ash and slag waste (in the descending by content order, light/heavy fraction, g/t): cerium (57,0/105,4), lanthanum (29,3/54,4), neodymium (23,5/45,9), praseodymium (5,37/10,6), samarium (4,95/8,60), gadolinium (4,60/8,77), dysprosium (4,17/7,71), erbium (2,78/4,91), ytterbium (2,75/5,40). Holmium, terbium, europium, lutecium and thulium are also found. Thus, it is vital to note that the heavy nonmagnetic fraction has concentration of the researched rare and rare earth elements; therefore, they are more associated with mineral components and less with the light fraction that is mainly represented with organic components. On top of research of waste composition of heat power industry with regard to the rare and rare earth elements, the authors of this work reasoned the theoretical mechanism of their mechanic and chemical activation with direct formation of necessary changes in physical and chemical characteristics of minerals and their associates for the purposes of intensification of the metal reclamation.

The reported study was funded by RFBR according to the research project № 18-29-24138.

REE-P4 Coal Ash Beneficiation Through Critical Material Extraction and Recovery

Clint Noack, Prachi Jain, Luke Meyers, Anactisis; Athanasios Karamalidis, Anactisis and Pennsylvania State University; USA.

Economics of ash harvesting, and reuse may be dramatically improved through the extraction and recovery of metals. Herein, we will present results of our on-going work to develop and commercialize a process for coal ash beneficiation through critical material extraction and recovery. These results will include characterization of metal leaching behaviors, adsorptive separation and recovery of these metals, and characterization of residual ash properties. Our results will show improvements on the state of the art with respect to target-metals selectivity, reagent consumption, and quality of residual ash. Metal recovery from fly ash by acid leaching has been studied extensively, however our technology addresses key weaknesses of prior attempts. In the past, separation technologies have been insufficiently selective, particularly with respect to Fe and Al. This required a number of costly and complicated stages of processing that relied on tight feedstock specs and process control. Our novel adsorbents allow much greater feedstock flexibility and tolerate greater ranges of feedstock variability. The second limitation of previous attempts has been the consumption of acid in the process. Typically, ashes are leached with a high strength mineral acid and then diluted or neutralized for compatibility with the separation chemistry of choice, be it precipitation, solvent extraction, or ion exchange. The complementary chemical mechanisms of our adsorbents allow for extraction and recovery without modification of the leachate chemistry.

REE-P5 Leaching Behavior of Rare Earth Elements from Anthracite Based Resources

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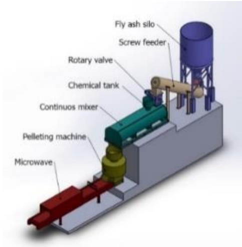
As rare earth elements becoming more expensive as the conventional ores are exhausted, and the demand has grown drastically, coal and its associated products are considered a promising alternative resource for these elements. This study focused on developing a leaching process to extract REEs from anthracite coal-associated clays with combustible carbon content varying from 8%-40% and total REE concentrations in the range of 300-350ppm on a whole sample basis. With NaOH hydrothermal treatment or thermal treatment at 750°C, the extraction levels of REEs were able to reach 35-80% for all three samples tested in this study, double the extraction levels compared to those of the untreated samples at various acid concentration levels (0.2-6M). The samples with higher recoveries were examined on an element-by-element basis and the recoveries for light REEs (LREEs) in both samples reached above 50%. After the thermal treatment, 90-100% of La, Ce, Pr, Nd, and Sm were recovered from one of the samples. With 6M NaOH hydrotreatment at 125°C for two hours, no significant difference was found in the recoveries between the coarse particles and the ultrafine ground particles with two hours acid contact time at various acid concentration levels. Citric acid at a lower concentration (5%) was also able to extract more than 55% of the total REEs with more than 70% of the high-valued Pr and Nd were extracted. This study demonstrated the feasibility of using low concentration acids to extract REE from low-valued coal-associated materials such as clays or ash generated in a typical fluidized bed combustion boiler. High extraction levels have been achieved for six (Ce, La, Pr, Nd, Eu, and Tb) out of the eight critical or near critical rare earth elements identified by DOE in 2011, suggesting a high economic potential.

CAM: COAL ASH MANAGEMENT

CAM-P1 Semi-Dry Geopolymer Fly Ash Pellet Accelerating the Polymerization Process of Fly Ash by Microwave

Nghia Trung Tran, Trung Hau LTD.; Minh Quang Do,
Ho Chi Minh City University of Technology; VIETNAM.

The study proposes a method, turning coal-fired power plants into "clean and green" power plants, by connecting the fly ash output of a thermal power plant to a system for handling large capacity of fly ash, producing compressed fly ash pellets with a diameter of 4-12 mm with arbitrary length. Hardness of these fly ash pellets can reach CBR 15+ (accordinh to ASTM D1883) which is suitable for materials for making roads, or can reach ASTM C330 which is the standard for lightweight aggregates used in concrete.
In this study, fly ash is used in a chemical reaction with alkaline activators to produce a new form of concrete, known as geopolymer concrete. The reaction time is shortened (only a few minutes) by using a technique of semi-dry pressing and microwave oven heating. The new binder formed by this method is tested by modern analytical methods such as Röntghen diffraction analysis (XRD), Infrared Spectrum (FTIR), and Scanning Electron Microscope (SEM). The result indicates that the geopolymer products with high or very high mechanical strength.



CAM-P2 Thermal Processing of CCR's

Rod B. Vera, Technologies International Corporation; Howard McClintic, CTC Foundation; USA.

An on-going problem for the U.S. electric power industry remains the coal combustion residuals (CCRs) that are by-products that result from coal's combustion to generate electricity. Currently, there are 676 coal combustion waste impoundments that are adjacent to existing coal-fired power plants and receive much of the 60 million tons that is produced annually. The average coal-fired power plant produces more than 540 tons per day (tpd) of coal ash that are mainly coal fly ash (47.9%), bottom ash (13.3%), flue gas desulfurization ("FGD") sludge (29.5%), and fluidized bed combustion ("FBC") ash (9.3%).

Depending upon the source and make-up of the coal being burned (i.e. bituminous, lignite, etc.), the main chemical composition can vary considerably. Both fly ash and bottom ash include substantial amounts of silicon dioxide ($SiO2$), both amorphous and crystalline, calcium oxide (CaO), which are both endemic in many coal-bearing strata, as well as aluminum oxide ($Al2O3$), and iron (III) oxide ($Fe2O3$). Further, certain CCRs contain more than 25% $FE2O3$. Significant quantities of magnesium oxide (MgO) are also present in most fly ash. Coal ash, depending on the specific coal bed source, can contain toxic constituents in varying amounts that include arsenic, beryllium, boron, cadmium, hexavalent chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium, along with dioxins and polycyclic aromatic hydrocarbons (PAH).

Technologies International Corporation (TIC) has developed a novel process for the conversion of wet CCR into saleable products by a thermal process, based on a modified electric arc furnace (EAF). This process allows for an efficient and cost-effective method for processing the CCRs at a cost of about $22 per ton. The thermal process converts the carbon into a syngas, which can be used to generate some of the energy used by the plant. The process also recovers the iron and other metals that may be found in the ash and can convert them to ingots for sale in the metals market.

At these very high temperatures, inorganic portions of the coal fly ash are converted into slag, a glassy ceramic/basaltic non-leaching, sand-like material, which immobilizes the heavy metals and prevents them from leaching out. In fact, the toxicity characteristic leaching procedure (TCLP) levels are several orders of magnitude below regulatory levels (previous tests show the material to be five times less leaching than bottle glass). The slag can be used as concrete aggregate and also is the building block of rock wool, which is used to produce insulation for buildings/homes (blown-in insulation and used in the production of ceiling tiles), the dashboards of automobiles as well as used in agriculture, as a growth medium in indoor farming/hydroponics. Rock wool is a chemically neutral substrate that has an optimum air to water ratio, making it a great growing medium.

TIC has been in existence for 10 years and holds 18 related patents. The process has zero air emissions. Nearly $9 million invested in TIC, including $1.25 million funding from DOE's NETL. This process can convert and dispose of all of the ash in an environmentally safe and cost effective ($22/ton) manner.

VA: VALUE-ADDED PRODUCTS FROM COAL

VA-P1 Efficient Process for the Production of High Conductivity, Carbon-Rich Materials from Coal

Dorin V. Preda, Min K. Song, Jake T. Herb, David P. Gamliel, Tyler R. Paul,
Christopher M. Lang, Physical Sciences Inc., USA.

Domestic coal can be used to manufacture high value carbon products for multiple applications. The market value of these high-performance materials often exceeds the fuel and heat value of coal, which illustrates there are sustainable market forces for manufacturing carbon materials from coal. Current processes to produce high performance carbon materials from coal pose significant challenges due to the high temperatures and corrosive reagents required to substantially modify the native coal structures. Under a DOE-sponsored program, Physical Sciences Inc. (PSI) developed and demonstrated an innovative approach for producing high value, carbon-based products from coal feedstocks. This paper will describe the approach and the key results. The innovation is a two-step process that generates both a high conductivity carbon material (HCCM) and valuable byproducts (mineral fractions for trace elements recovery and low emission fuels). PSI demonstrated: (1) a robust and scalable process to produce the target carbon product with appropriate surface area (>50 m^2/g) and low mineral content (Fe<100 ppm); (2) High performance battery electrodes utilizing the PSI HCCM; and (3) economic feasibility for scale up and commercialization. The paper will provide a comprehensive overview of the overall process that provides economical production of high conductivity carbon materials for electrochemical applications. The production of valuable byproducts will also be discussed.

VA-P2 Product Distributions and Characterizations for Integrated Mild-Liquefaction and Carbonization of Low Rank Coals

Sheng Huang,Yanling Li, Youqing Wu, Shiyong Wu, Jinsheng Gao, East China
University of Science and Technology, CHINA.

In order to realize the efficient conversion of low-rank coals, an integrated mild liquefaction and carbonization (IMLC) technology was proposed, and the effects of carbonization temperature (CT) on the product distributions and characteristics from the simulated IMLC technology was investigated. Results show that about 30.34−40.02% of liquid products (LPs) and 40.64−56.25% of semicokes (SCs) can be obtained from the IMLC process at the CT of 410−600 °C. The adopted carbonization process is an effective measure to separate the solid and liquid products from the coal liquefaction process, and the obtained SCs contain no n-hexane soluble fractions (HSs). The LPs present a quite high HS content (82.20−90.80%) and a small quantity of asphaltenes and preasphaltenes, and the HSs are predominantly abundant with aliphatics, alkyl benzenes, and alkyl naphthalenes, indicating that the LPs are potentially suitable for utilization to produce liquid fuels by further refining. The obtained SCs could be used as a binder to reduce the use of high-coking coals in the coke-making of coal blends or as fuel of boilers to substitute for anthracite, depending on the conditions of the carbonization process. The proposed IMLC process could realize the economic and efficient conversion of low-rank coals into LPs and SCs under mild conditions.

University-Industry Fossil Energy Forum

Wednesday, September 4, 2019

10:30 am - 12:30 pm

The 36th Annual International Pittsburgh Coal Conference is proud to present for the first time the **University-Industry Fossil Energy Forum**. The forum is an open discussion and information exchange between universities and industries on their roles in meeting national/global needs. The focus of this first Forum is to improve the collaboration between US universities and industries in responding to workforce needs, conducting joint research, and providing recommendations to governmental units regarding the use of coal, natural gas, and petroleum (and products related to these resources). In future Forums, the program will include an international focus.

This Forum will be moderated by **Prof. Richard A. Bajura**, Director Emeritus, National Research Center for Coal and Energy (NRCCE), West Virginia University.

The **University-Industry Fossil Energy Forum** participating panelists are:

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Associate Vice President for Research Development / Director, Kentucky Center for Applied Energy Research
University of Kentucky

Ms. Shannon Angielski
Executive Director
Carbon Utilization Research Council

Mr. Daniel Connell
Vice President, Business Development & Technology
CONSOL Energy, Inc.

Prof. Ben Ebenhack
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The poster session is scheduled for 17:15 on Thursday, September 5, 2019. The Conference will provide boards/ easels for poster setup.

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Hosted by:

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Location: Westin Convention Center Hotel,

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Date: September 8-11, 2020

Abstracts must be submitted by March 1, 2020. Please submit a one-page abstract, including title, topic area, authors, affiliations, and contact information via a valid email address to: Conference Office: ipcc@pitt.edu

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