Advanced Coal Technology Consortium Fact Sheets

DECEMBER 2015

U.S.-China Clean Energy Research Center

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This document contains factsheets for the eight research themes of the Advanced Coal Technology Consortium, and, within these themes, factsheets for significant subtasks/projects that were conducted during the last 15 months of CERC Phase I (October 2014-December 2015).Titles denoted with an asterisk (*) indicates themes in which the factsheet was last updated in November 2014. All other factsheets provided in this document are up-to-date through December 2015, the conclusion of Phase I.

Advanced Power Generation*

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U.S. Partners
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- Tsinghua University
- Shanghai Jiao Tong University
- Harbin Institute of Technologies
- Huaneng Clean Energy Research Institute
- China Power Investment Corporation
- China Power Engineering Consulting Group Corporation
- Shenhua Group

Research Objective

The researchers are pursuing activities that will lead to a breakthrough in advanced coal generation and applications of key technologies. There are three categories within this research topic:

Upgrade pulverizing system for subcritical power plants

- Evaluate potential improvements of coal pulverizers in coal-fired power plants (CFPPs) in China and the United States
- Identify target units from CFPPs with a coal classifier
- Improve fundamental understanding of dense fluid flows so as to lower NO_x emissions

Advanced ultra-supercritical (A-USC) power generation

- Conduct research on combustion and heat transfer characteristics of large-capacity and high-parameter boilers
- Study the combustion and heat transfer characteristics of super 700°C A-USC boilers
- Establish a prediction model for ash deposition, and provide quantitative data for fine particle removal and ash deposition prevention

Improve efficiency, availability, and emissions reduction of existing CFPPs

- Obtain detailed data related to increasing efficiency and carbon reduction for different boiler types, loads, and coal types for in-service power plants
- Evaluate the retrofitting technologies and obtain the technological roadmap for increasing efficiency and pollutant emission reduction
- Obtain the retrofitting and operation experience of key technologies

Technical Approach

The technical approach for this project contains three categories:

Upgrade pulverizing system for subcritical power plants

- Survey the modification of coal pulverizers in CFPPs in China and the United States
- Evaluate potential improvements, including different configurations of coal mills and the pulverizing system
- Identify target units from CFPPs with a coal classifier
- Use a classifier lab rig in Beijing and modeling in Beijing and in WVU to improve fundamental understanding of dense fluid flows

* *Factsheet last updated November 2014*

A-USC boiler development

- Conduct research on a thermodynamic system of 700°C A-USC units combusting Xinjiang coal
- Design a system for 700°C A-USC boilers combusting Xinjiang coal
- Conduct research on heat transfer and hydrodynamics of 700°C A-USC boilers
- Conduct research on fouling and slagging characteristics of 700°C A-USC boilers

Improve efficiency, availability, and emissions reduction of existing CFPPs

- Survey operation of existing CFPPs that have adopted efficiency improvement technology both in China and the United States
- Identify one or two specific units (e.g., 300–600 megawatt electrical [MWe]) with similar characteristics in both countries
- Analyze the operational characteristics and cycling behaviors of these plants and conduct a performance diagnosis
- Evaluate the potential for efficiency improvements and emission reduction
- Develop a final toolbox for both China and the United States to use in improving CFPPs
- Use CFD to study the effects of coal type and coal pulverization fineness on boiler emissions

Recent Progress

In 2012, research focused on investigating the combustion of Xinjiang Houxun coal in A-USC boilers. Fundamental experiments were conducted on coal with severe combustion characteristics. The development of improved A-USC boiler technologies was adopted as a national program by China. Also in 2012, LP Amina was able to investigate the current fuel processing system distribution in the United States. Further details on research progress include the following:

- Gathered statistics about type of unit, number, and capacity of CFPPs in China through a survey. The data showed that by the end of 2009, subcritical power plants account for 78% of the coal-fired fleet, while supercritical and ultra-supercritical units make up the remaining 22%. It was determined that the target plant for detailed investigation will be a subcritical unit with a capacity range from 300–600 MWe
- Finalized the benchmark investigation survey for the target CFPPs, with the following parameters necessary for a complete investigation: design parameters such as steam parameters, furnace and burner design, pulverizing system characteristics, flue-gas temperatures, and soot blowing system details; operational parameters such as heat rate, excess air, and load factor; and information about installing existing energy conservation and emissions reduction technologies such as soot blowing
- Carried out research on pulverized coal combustion in counterflow flames quite successfully. Accomplished the design, processing, assembly, and preliminary test of the first-of-a-kind experimental system

Figures 1 and 2. Particle behavior during flame penetration is visible.

- Studied the ignition in the Hencken burner and investigated different ignition mechanisms, ignition characteristics with a thermogravimetric analyzer/wire mesh reactor, and burnout properties of mixed coal. The research of A-USC power generation was combined with an investigation of the characteristics of Xinjiang coal. Research on combustion and hydrodynamic coupling characteristics of an A-USC boiler was performed. Theoretical modeling and numerical simulation of the aerial dynamic field, temperature field, and combustion efficiency of an A-USC boiler was completed. Construction of an experimental platform designed to investigate the combustion and hydrodynamic coupling characteristics of a 0.3 megawatt A-USC boiler is in process. The team also conducted an investigation on the transformation of minerals in combustion and the characteristics of soot heat resistance. The

influence of fouling and slagging on the heat resistance of the heating surface was studied. To identify a methodology for predicting and controlling fouling and slagging, quantum chemistry was introduced

- Investigated the transformation of minerals in combustion and the characteristics of soot heat resistance. The influence of fouling and slagging on the heat resistance of the heating surface was studied. To identify a methodology for predicting and controlling fouling and slagging, quantum chemistry was introduced
- Investigated the influence of the pulverizing system on NO_x emission; researchers noted that the characteristics of the fuel, the primary air, and the combination of the air and fuel are the dominant influences. Factors such as the oxygen concentration in the burner zone and temperature in the burner zone also affect the emission of NO_x

Expected Outcomes

The research team's efforts in A-USC power generation will produce a thermal calculation method of large-capacity and high-parameter boilers, a general large-capacity boiler thermal calculation program module, a calculation method of furnace combustion and heat transfer for super 700°C A-USC boilers, heat transfer coupling characteristics between the furnace and the pipe of USC boilers, and a prediction model of ash fouling and slagging in A-USC boilers.

Clean Coal Conversion Technology*

U.S. Research Team Lead
- West Virginia University

U.S. Partners
- LP Amina
- National Energy Technology Laboratory
- Lawrence Livermore National Laboratory
- University of Wyoming
- University of Kentucky

China Research Team Lead
- Zhejiang University

China Partners
- Shenhua Group
- China University of Mining & Technology
- ENN (XinAo Group)
- China Academy of Sciences

Research Objective

Collaborative research teams from the United States and China are performing research and development (R&D) of new coal co-generation systems with CO_2 capture, including new coal-to-chemical co-generation; new CO_2 capture processes; and co-generation systems with combined pyrolysis, gasification, and combustion. Specifically, the team will accomplish the following:

- Develop and deploy a new poly-generation technology to reduce waste heat, water utilization, and greenhouse gas emissions while improving thermal efficiency in utilization of coal to produce power and chemical by-products
- Design and build a demonstration coal-to-chemicals poly-generation plant in China under the leadership of LP Amina to demonstrate the new poly-generation technology
- Conduct R&D of new coal co-generation systems with CO_2 capture, including new approaches for coal-to-chemical co-generation
- Develop advanced gasification catalysts and concepts

Figure 1. Coal-fired furnace.

Technical Approach

Researchers from both countries are working together to develop new technology to convert conventional power plants into poly-generation plants that make full use of waste heat and oxy-fuel combustion to produce chemicals and further polymers from coal. The approach leverages investments in technology development and industrial implementation aimed at reducing emissions, improving efficiency, and increasing economic benefits associated with coal power production. The technical approach includes the following:

- Build a laboratory-scale research facility
- Develop a new carbothermic reduction process to produce standard industry chemicals from limestone and coal
- Produce synthetic chemicals and fuels

* *Factsheet last updated November 2014*

This research will result in the development of a demonstration project at a power plant in Shanxi, China, by LP Amina. In addition to standard engineering analysis, this work will require a substantial amount of basic research, especially in system analysis, reactor dynamics, chemical kinetics, emissions, and process stability and reliability.

Recent Progress

Researchers from the Chinese and U.S. teams have carried out the related R&D efforts smoothly and achieved meaningful progress on co-generation system combined pyrolysis, gasification, and combustion; chemical looping gasification with CO_2 capture; direct synthetic natural gas (SNG) production from coal; gasification properties of the coal direct liquefaction residue; measurement, modeling, and environmental technologies for unconventional coal gasification; and the coal/biomass co-conversion process. Researchers have accomplished the following major achievements:

- Validated coal co-generation technology combined pyrolysis, gasification, and combustion on a 1-megawatt thermal pilot plant; this technology may be demonstrated in industry
- Completed commissioning tests of the constructed ~15 kilograms/hour chemical looping gasification facility and validated the coal chemical looping gasification technology approach
- Obtained coal gas with high-concentration CH_4 from the constructed bench-scale high-pressure constant volume reactor, which validated the possibility of direct SNG production from coal
- Confirmed the feasibility of liquefaction residue for coal gasification and developed suitable additives for coal liquefaction residue and coal mixture slurries
- Utilized a model underground coal gasification test reactor to evaluate the temperature and concentration fields and to draw a model of the cavity
- Developed the key processes and efficient catalyst for co-transformation of biomass and coal based on the constructed experimental platform
- Developed a chemical kinetics model for calcium carbide production, as well as a slag flow model for use with oxy-coal combustion reactor simulations
- Explored effects of temperature and exposure time on the gasification kinetics of Powder River Basin (PRB) coal
- Explored catalytic methods for production of ethylene glycol from coal syngas, including development of a method for catalyst production

Expected Outcomes

The implementation of poly-generation will reduce capital costs, greenhouse gas emissions, and plant maintenance costs of power generation sites. When paired with cleaner coal utilization with increased efficiency and minimal waste, poly-generation will be a cost-effective, commercially viable option for reducing CO_2 emissions in the power generation sector. This approach will also enable minimization of waste heat and/or materials. The LP Amina-Gemeng International Energy plant could reduce greenhouse gases by more than 25% compared to conventional technology. Newly developed catalysts and processes will enable efficient conversion of coal to syngas and related by-products.

Coal Conversion and Utilization

Collaborative Project

U.S. Research Team Lead

- **West Virginia University**

U.S. Partners

- **University of Wyoming**
- **LP Amina**

China Partners

- **Zheijiang University**
- **Gemeng International Energy**

Overview

This Report is on Design and simulations very high temperature oxy-coal reactors to produce higher valued products such as Calcium Carbide. The primary objective of this project was to enable and transform the technology for production of Calcium Carbide (CaC_2) from coal and lime (CAO) using oxy-combustion to achieve the necessary high reaction temperature greater than 1600°C.

Research Objectives

- Develop computational fluid dynamics (CFD) models for, and conduct simulations of calcium carbide production from coal and lime within the slag layer of an oxy-coal fired slagging reactor, including development of a slag flow model.
- Conduct experiments to determine the solid state reaction kinetics of the formation of calcium carbide from coal and lime in conventional and microwave furnaces.
- Design a down-fired, entrained-flow oxy-coal reactor for production of calcium carbide.
- Develop kinetics model of calcium carbide formation from coal and lime.
- Conduct CFD simulations in support of LP Amina's carbide-reactor development activities.
- Develop a bubbling bed reactor with submerged combustion for production of calcium carbide.

Summary of Research Activities

SUMMARY OF TASKS

Research focused on investigating the feasibility of conversion of coal to higher value chemicals, namely the production of calcium carbide from coal and lime. The research efforts carried out include both conducting fundamental experiments on calcium carbide formation in lab-scale furnaces, and the development of simulation tools to assist with the design of calcium carbide reactors. Further details on research progress include the following:

Modeling and Simulation (calcium carbide formation):

- Conducted an extensive review of existing literature related to the chemical kinetics of calcium carbide formation. The findings reported by the previous

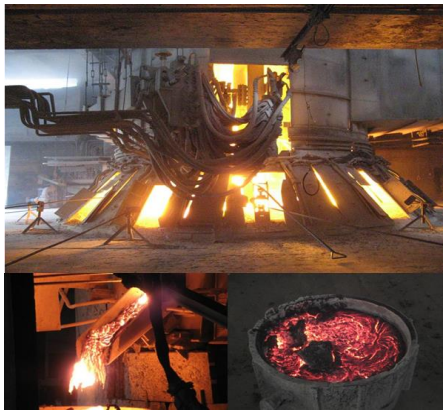

Figure 1: Conventional coal-based PVC production process using electric arc-furnaces

Figure 2: LPA-WRI (LP Amina CTC reactor) Facility, Laramie, WY

authors were used to conduct a survey of the applicability of existing kinetic rate models. This survey determined that the existing models were not appropriate to formation of calcium carbide, thus a new "multi-step reaction model" was developed for use with CFD simulation of calcium carbide reactions within a liquid layer of coal slag.

- A Reduced Order Model (ROM) for oxy-coal combustion was developed for quick prediction of reactor flue gas temperature and composition. The primary use of this model was for the determination of required reactor operating conditions to achieve the desired reactor temperatures without conducting more resource- and time intensive CFD simulations. Validation of ROM results against CFD simulations showed matching of key integral design parameters to within +/- 3% of CFD simulation results.
- Designed a Very High Temperature Entrained Reactor (VHTER) for calcium carbide, and conducted CFD simulations of reactor performance. The VHTER design was a modular down-fired, swirling entrained reactor capable of operating wall temperature as high as 2000-2200˚C.

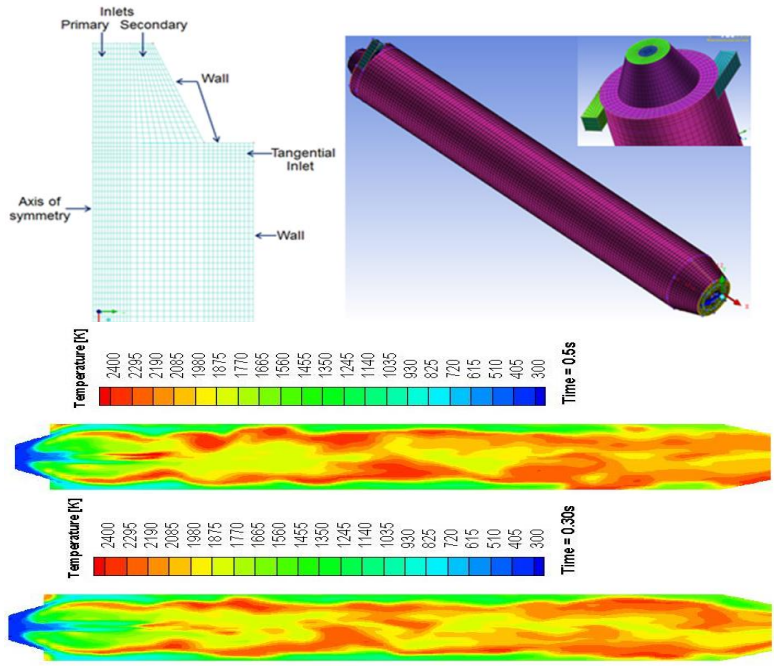

Figure 3: a) Geometry and b) Temporal temperature contours of Very High Temperature Entrained Reactor (VHTER) Designed at WVU, key accomplishments in modelling and simulation: 1) Designed and assessed the performance of 100kW down-fired oxy-coal combustion reactor. 2) Developed a slag model with chemical reactions within the slag layer. 3) Developed a kinetics model for formation of calcium carbide from coal and lime. 4) Studied chemical equilibrium of calcium carbide formation in slag.

- Conducted fundamental CFD simulations of oxy-coal combustion in down-fired entrained reactors, and validated the simulation results against previous literature.
- Developed a model for the simulation of slag flow along the walls of an oxy-coal combustion reactor. This model incorporated the multi-step reaction model developed by the WVU research team for carbide production. Additionally, the model included functionality for calculating solidification rates and eutectic formation.
- A preliminary study of chemical equilibrium conditions for carbon and lime (CaO) in coal slags containing iron, aluminum and silica oxides was conducted. The results of this study suggested that the calcium oxide preferentially formed complex compounds with the various metal oxides prior to formation of carbide, requiring additional CaO be present for carbide formation within the slag layer.

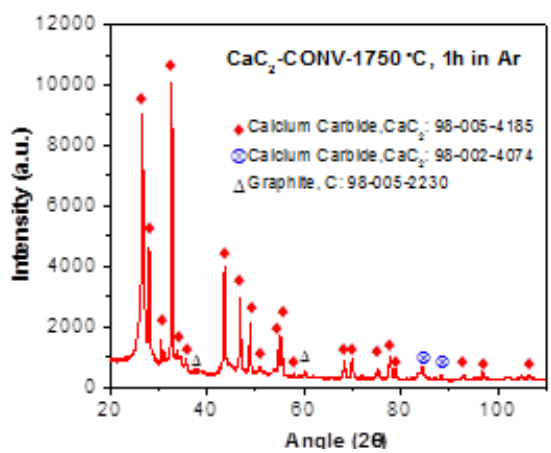

Figure 4: X-ray analysis of CaC_2 synthesized from spring creek coal char and lime (CaO) in 3:1 ratio and conventionally heated at 1750 ºC for 1h in flowing Argon.

Experiments in Solid State Formation of Calcium Carbide

- Conducted experiments for calcium carbide formation from finely-ground carbon and lime using both a conventional tube furnace, as well as a novel microwave furnace.
- Calcium carbide yields were compared for a range of temperatures and exposure times at given temperatures.

Additionally, reactor yield comparisons were carried out between the conventional tube furnace and the microwave furnace.

- The results were analyzed and assessed to determine reaction and conversion rates as a function temperature and composition

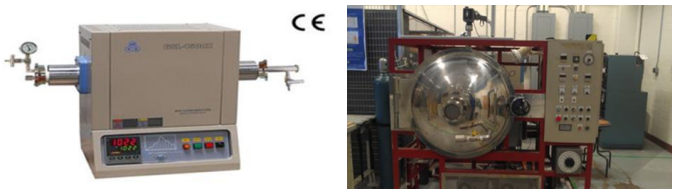

Figure 5: Nabertherm high temperature tube furnace (Left); Hadron Industries 2.45gHz microwave furnace (Right). The furnaces are compared for calcium carbide formation. Experiments carried out using graphite, coal and coal char. Microwave furnace measurements showed more complete conversion to calcium carbide in less time and lower energy requirements compared to the conventional tube furnace.

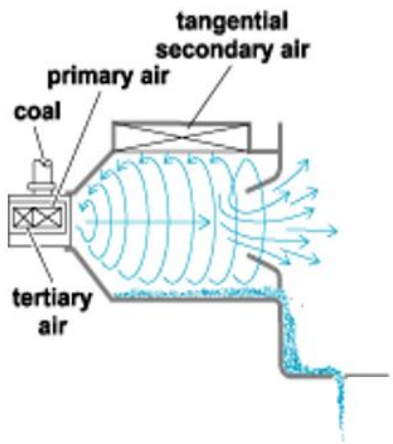

Figure 6: Schematic diagram of cyclone furnace: Advantages include: 1) tolerates high amounts of solids, 2) coal and lime particles can achieve temperatures approaching 1800 C, 3) air-fired walls can be cooled to utilize waste heat for steam generation, 4) solidified slag on walls can protect

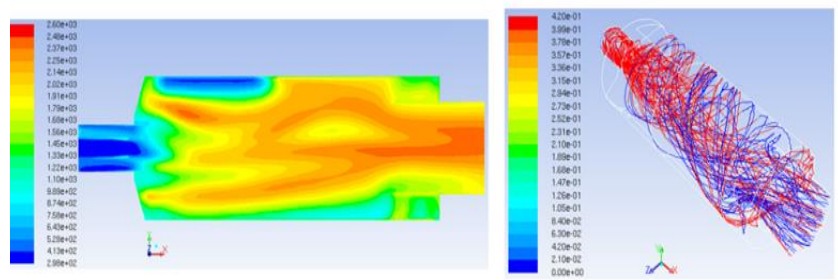

Figure 7: CTC reactor CFD results of temperature contours and particle trajectories (showing extent of char burnout) for a low temperature simulation case. Specified operating conditions for this case lead to unstable combustion and wall temperatures too low for initiation of calcium carbide production within the slag layer.

MAJOR FINDINGS AND OUTCOMES

Kinetic rates measured as part of this task for calcium-oxide Coal/char reactions can be used to study high conversion processes other than carbide production. The physics-based slag flow model developed including internal reactions of CaO and Coal/carbon in presence of other impurities will prove to be an invaluable tool for the design of future poly-generation reactor systems that utilize liquid slag as a medium for the conversion of coal to higher value products. This model can also be used in the design of other coal-fired reactors and boilers in which control of slag deposition and formation on reactor surfaces is of critical importance.

Additionally, the preliminary experimental results for the formation of calcium carbide via microwave processing shows great promise that further development of this technology may very well lead to production methods that are superior to the current use of electric arc furnaces. Furthermore, the proposed bubbling reactor concept with submerged combustion of coal has high potential for efficient production of higher valued product from coal.

Table 1: CFD Results for different operation conditions below aimed at obtaining higher wall temperatures

Case ID	Air (PA)	Coal (PA)	CaO (PA)	Air (SA)	O2 (SA)	NG (SA)	T(K) (PA)	T(K) (SA)	Avg.-T_{wall}(K)
CTC-03-31-15	24.16	17.3	0.82	119.57	8.89	2.23	298	784	1800
CTC-48	24.16	17.3	0.82	119.57	15.56	3.9	298	784	1900
CTC-49	24.16	17.3	0.82	119.57	15.56	3.9	298	900	2100
CTC-52	24.16	17.3	7.48	104.67	22.23	6.69	298	900	2250

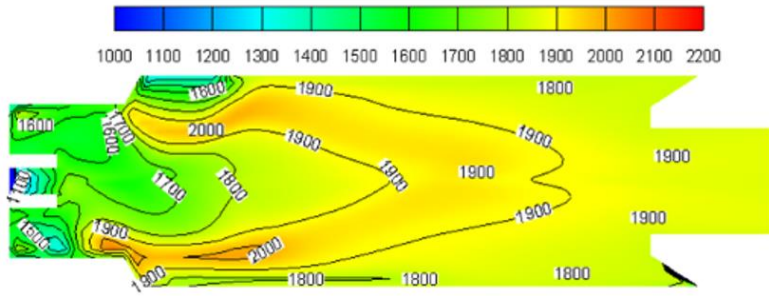

Figure 8: Temperatures contours for CTC shown in degree Kelvin (K) for the case of CTC-03-31-15. Results show that temperatures approaching the range required for carbide formation (1750°C-1800°C) were achieved. Analysis and computer simulation by various means determined that achieving 100°C higher temperatures would be beneficial in increasing carbide yield. Oxy-fired tests demonstrated the feasibility of oxy-thermal carbide production with further modification of reactor hardware (See also Table 1.

Figure 9: LP Amina's demonstration facility in Shanxi, China. Groundbreaking design will allow the power plant to co-produce electric power and high value bi-products, increasing revenues and cutting emissions.

Major Achievements

- Dr. Celik's research team at WVU designed and analyzed a very high temperature (1700-1800°C) oxy-coal combustion reactor favorable for production of Calcium Carbide from coal and limestone. Another reactor that was designed and patented by LP Amina (namely, the CTC Reactor) for the same purpose, was also analyzed using computational fluid dynamics (CFD) tools and models. Both reactors were rated at c.a. 100 kW power output. CFD simulations for the first reactor indicated that it met all expectations except the slag-flow residence time, which was relatively short due to very high temperatures, hence low slag viscosity. The second reactor was built, and tested at Western Research Institute (WRI), University of Wyoming by LP Amina. Temperature data collected from the CTC reactor matched the CFD predictions of the WVU team, which indicated that the overall slag temperature was relatively low to activate appreciable Calcium Carbide production. The WVU team performed further simulations and made recommendations to increase Calcium Carbide production rates within the CTC Reactor.
- The WVU team measured kinetic reaction rates in a high temperature tube furnace and used for model validation. The team also investigated alternate ways of producing Calcium Carbide using coal as the raw material. Experimental results using a micro-wave furnace showed the conversion could be completed in much shorter time at the same temperature. A second alternative is proposed whereby coal and limestone can be reacted in a bubbling slurry reactor with submerged combustion. Three phase (gas-solid-liquid) flow experiments with melting of wax demonstrated high rates of mixing, which is necessary for faster chemical reactions. To this end an IP disclosure has been filed with the WVU Technology Transfer Office.
- In parallel to the above research efforts, LP Amina has signed an agreement with the Chinese company, Gemeng International Energy (GMIE), to build a poly-generation power plant which will enable full-scale application of this technology. LP Amina also built a 25 MW unit in Shanxi, China as a retrofit to a PCB, which is currently being tested.

Economic analysis indicate that this technology can reduce green-house gases by at least 25% compared to electric-arc-furnace technology, while at the same time reducing energy consumption and waste heat simultaneously.

IP Disclosures

- Celik, I. B., Rowan, S. L., Johnson, E.K., Ravinuthala, S.C., 'Three-Phase Bubbling Bed Reactor with Submerged Combustion for Coal-to-Chemical Conversion Processes.' I.P. Disclosure paperwork submitted to WVU Office of Tech Transfer, September 2015.

Workshops

- Workshop on Co-Generation Sub-Topic: Chemical Looping Overview, Organized by Prof. I. Celik (WVU) Prof. Z. Luo (ZJU) and Dr. G. Richards (NETL), Morgantown WV, August 2010.
- CERC-ACTC Mini-Symposium on Coal Conversion & Utilization (Theme-2), Organized by Prof. Q. Wang (ZJU), Prof. Z. Luo (ZJU), and Prof I. Celik (WVU), Hangzhou, China, September 2014

List of Publications

- Rowan, S., Celik, I., Gutierrez, A., Escobar, 'J. A Reduced Order Model for the Design of Oxy-Coal Combustion Systems.' Journal of Combustion, October, 2015.
- Pillai, R.C., Sabolsky, E.M., Rowan, S.L., Celik, I.B. and Morrow, S., 2015. 'Solid-State Synthesis of Calcium Carbide by Using 2.45 GHz Microwave Reactor'. Industrial & Engineering Chemistry Research, 54(44), pp.11001-11010.
- Gutierrez, A., Rowan, S., I. Celik. 'Slag Flow Modeling With Reactions in Oxy-Coal Combustors.' International Pittsburgh Coal Conference. Pittsburgh. 2014.
- Rowan, S., Gutierrez, A., I. Celik. 'A Reduced Order Model for the Design of Oxy-Coal Combustion Systems.' International Pittsburgh Coal Conference. Pittsburgh. 2014.
- Rowan, S.L., Wu, F., Celik, I.B., Weiland, N.T., 'Experimental Investigation of Char Generated from Co-Pyrolysis of Coal and Appalachian Hardwoods,' Fuel Processing Technology. 2014, 128, 354-358.
- Rowan, S.L., Celik, I.B., Escobar Vargas, J.A., Pakalapati, S.R. and Targett, M., 2014. 'Reaction kinetics modeling of CaC2 formation from coal and lime.' Industrial & Engineering Chemistry Research, 53(8), pp.2963-2975.
- Rowan, S.L., Celik, I.B., Escobar Vargas, J.A., Pakalapati, S.R., Targett, M., 'Sensitivity Analysis of the Multi-Step Reaction Model for CaC2 Formation from Coal and Lime,' 30th International Pittsburgh Conference, September 15-19, 2013, Beijing, China.
- Iyere, P.E., Rowan, S. L., Sabolsky, E.M., Celik, I.B., Sabolsky, K., Targett, M., Morrow, S., 'Solid State Synthesis of Calcium Carbide.' 30th International Pittsburgh Coal Conference, September 15-19, 2013, Beijing, China.
- Rowan, S., Olajide, O., Wu, F., Celik, B. and Weiland, N., 'Experimental Evaluation of Co-Pyrolysis of Coal and Appalachian Hardwoods.' International Conference on Coal Science and Technology, September 30-October 3, 2013, State College, PA.
- Gutierrez, A., Rowan, S., I. Celik. 'An Integrated Approach for the Design of a Pilot Scale Oxy-Coal Combustion Reactor Using CFD and Chemical Equilibrium Software.' Technical Meeting of the Combustion Institute. Clemson. 2013.
- Gutierrez, A., Posada, A., I. Celik. 'CFD Study of Oxy Coal Combustion in a 100kW Down-Fired Furnace.' International Pittsburgh Coal Conference. Pittsburgh. 2012.

Commercialization

The research will inform the design of very high temperature poly-generation reactors, in general, in particular, provided valuable insight into problems that may be encountered while operating coal-based reactors at temperatures greater than 1700˚C. Further pilot scale tests supported by multi-dimensional computer simulations are needed to increase the potential for commercialization at full scale in China's coal-to-chemicals markets.

Collaboration

The Industry partner, LP Amina, has provided background and patent information for the aforementioned technology. The WVU research team and industry researcher met frequently (once a month) to discuss progress and future tasks and exchanged technical information. The industry partner also participated in the research by building a lab-scale

demonstration unit and conducting tests at Western Research Institute (Univ. Wyoming). The experimental data was shared with WVU researchers and used for model validation.

Under this particular sub-task there was cooperation with Zheijiang University (ZJU), in terms of exchanging visiting scholars and students, as well holding joint workshops on topics of mutual interest. Our industrial partner has also collaborated closely with Chinese industry to perform pilot scale tests and build demonstration units.

Conclusions

Researchers at WVU have performed high fidelity, CFD (computational fluid dynamics) simulations to predict temperature field, species concentrations and conversion rates. The CFD model needed reaction mechanisms and corresponding reaction rates which were obtained also by WVU research team using a high temperature furnace reactor and a micro-wave furnace. Laboratory testing performed by LP Amina and WRI researchers with a 100KW slagging cyclone reactor (CTC reactor) showed promise even at temperature of 1700°C. Further simulations of the CTC reactor showed that higher temperatures can be attained using natural gas assisted coal-combustion, which in turn would increase production rates and the efficiency.

Overall, oxy-fired laboratory tests and CFD simulations demonstrated the feasibility of oxy-thermal carbide production with further modification of the reactor hardware. However, it should be noted that the carbide formation kinetics experiments revealed that a number of by-product conversion pathways are possible, leading to consumption of carbon and CaO to form non-calcium carbide bearing product materials. These pathways were also predicted by thermodynamic simulation. For example, non-calcia bearing components in the molten slag, such as alumina and silica and iron oxides, were shown to be reactive with carbon in the slag in varying degrees, limiting the amount of carbide formation.

Alternative ways of Carbide production (a) using microwave furnace, (b) using bubbly reactors with submerged combustion were investigated and found to be promising.

Pre-Combustion CO_2 Capture*

U.S. Research Team Lead

- David Julius, Duke Energy

U.S. Partners

- Duke Energy
- General Electric
- Lawrence Livermore National Laboratory
- West Virginia University

China Research Team Lead

- XU Shisen, China Huaneng Group Clean Energy Research Institute

China Partners

- China Huaneng Group Clean Energy Research Institute
- Tsinghua University

Research Objective

The development and implementation of the integrated coal gasification combined cycle (IGCC) into power generation is still in the first-of-the-kind stages. In this theme, industrial, research, and academic leaders from both the United States and China will work with industrial-scale demonstration projects and best-in-class technologies to provide the world with robust, transparent cost and performance estimates for IGCC power plants with carbon capture and storage (CCS).

This project has one primary goal: development of techniques to aid in the design and optimization of commercial-scale IGCC systems. Specifically, the team will accomplish the following:

- Assess the economic feasibility and operability of gasification technologies in conjunction with the removal of criteria pollutants
- Assess the technical/economic feasibility and operability of novel carbon capture technologies
- Optimize the economics of different carbon capture technologies
- Establish guidelines/protocols/criteria for system optimization and evaluation, as well as techno-economic analysis and comparison at commercial-scale application

Technical Approach

The project emphasizes system integration, optimization, and key component development. The technical approaches for the project's two tasks are the following:

Development of techniques for integration and optimization of an IGCC system

- Study the integration, optimization, and modular design of an IGCC system based on the existing research and demonstration experience of the first IGCC plant in China, as well as the experience of both existing and under-construction IGCC in the United States

Understand the key components in a pre-combustion CO_2 capture process

- Design and construct the slipstream-scale pre-combustion CO_2 capture and utilization system by extracting a slip-stream syngas from an existing IGCC plant

To accomplish this work, researchers (led by the China Huaneng Group and assisted by Duke Energy in the United States) will develop techniques for the optimization and design of a commercial-scale IGCC system based on the existing research and demonstration experience of GreenGen, the first IGCC plant in China, and the experience of IGCC at Duke Energy's Edwardsport Station.

The major obstacles the two companies have been trying to work through include various intellectual property issues and other legal issues with the partners providing the technology.

* *Factsheet last updated November 2014*

Researchers (led by Huaneng) will also develop advanced key components, including pre-combustion CO_2 capture featuring heat-integrated, robust, ultrathin barriers with reasonable contamination resistance to flue gas; advanced water-gas shift reactors; advanced separation reagents; and advanced compression technology.

The ACTC team's specific activities that further pre-combustion CO_2 capture will include the following:

- Developing and fabricating heat-integrated, robust, ultrathin barriers with reasonable contamination resistance to flue gas for both pre- and post-combustion CO_2 removal
- Formulating new CO_2 absorbents with chemical additives for pre- and post-combustion CO_2 capture with high capacity, fast kinetics, and high stability
- Initializing models for existing pre-combustion capture technologies, chiefly physical sorbents, both as individual models and within the two reference plants (including water-gas shift and gas cleanup)

Recent Progress

Duke Energy's Edwardsport plant and Huaneng's GreenGen IGCC reached an agreement on the reporting format and identified that information regarding the following example areas will be exchanged:

- Air separation unit
- Gasification
- Power block
- General utilities and common systems
- Environmental performance
- High-level costs
- Start-up report

Both companies would prefer to hold a workshop at each owner's IGCC site, as well as to develop a long-term IGCC technology-sharing relationship. There are significant intellectual property issues that will need resolution before a long-term agreement can be developed.

The ACTC team's specific progress for pre-combustion CO_2 capture research includes the following:

- Completed the comparison, selection, and unit modeling of a 30 megawatt thermal (MWth) pre-combustion CO_2 capture system
- Completed the process flow diagram, which includes the equipment layout, process equipment tables, major static equipment diagrams, and system control program. Completed the key equipment design of a 30 MWth CO_2 capture system based on IGCC

- Completed the capture reagent and process development evaluation. Confirmed the best adsorption temperature and the fittest CO_2 concentration of $CaCO_3$ and CaC_2O_4 as precursors

Figure 11. China Huaneng GreenGen IGCC.

- The high-temperature, solid-state method is used to modify the adsorbent by doping magnesium, aluminum, cerium, zirconium, and lanthanum. The team found that the adsorption capacity was dependent on different conditions

Expected Outcomes

Key outcomes will include critical data, lessons, and knowledge shared through operational experience with demonstration projects as systems are optimized and the cost of pre-combustion CO_2 capture is lowered. Such knowledge sharing contributes to accelerating the development of IGCC with CCS, a critical pathway toward low-carbon power generation with coal.

Post-Combustion CO_2 Capture*

U.S. Research Team Lead

- University of Kentucky, Center for Applied Energy Research

U.S. Partners

- Los Alamos National Laboratory
- Lawrence Livermore National Laboratory
- Duke Energy

China Research Team Lead

- China Huaneng Group Clean Energy Research Institute

China Partners

- Tsinghua University
- China Power Engineering Consulting Group Corporation
- China Power Investment Corporation

Research Objective

The goal of this task is to integrate advanced capture and solvent technologies into the development of efficient CO_2 capture. Parts or combinations of these technologies will be used to lower the energy costs related to a post-combustion capture process.

The Advanced Coal Technology Consortium (ACTC) team is directly addressing the need for steep emissions reductions from the existing coal fleet by analyzing, testing, and demonstrating technologies for post-combustion capture integrated with sequestration (e.g., storage) at real power plants. Through streamlined bilateral joint cooperation, U.S. and Chinese researchers are looking to accomplish the following:

- Research efficiency improvements for affordable post-combustion CO_2 capture technologies
- Coordinate efforts between U.S. and Chinese partners
- Develop models for post-combustion CO_2 capture, utilization, and storage (CCUS) technology at a commercial scale

Technical Approach

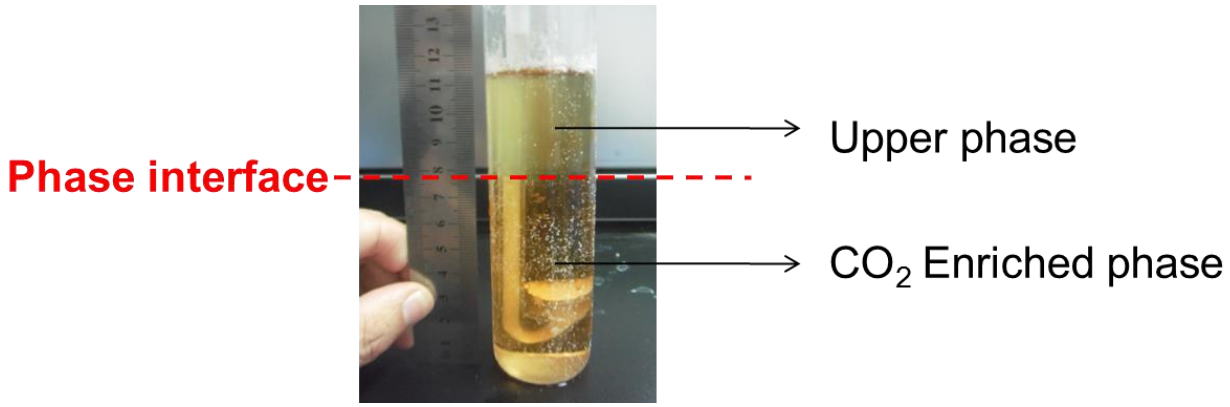

Figure 1. Biphasic solvent demonstrating a CO_2-enriched phase lowering the liquid load during desorption in the stripper.

To enable commercial-scale CCUS, the ACTC team is addressing the gap between theoretical energy requirements for post-combustion capture and present-day commercially available technologies. The team's technical approach includes the following:

- Conduct a pre-engineering study of the 1 million tons/year post-combustion CO_2 capture systems, combined with a preliminary techno-economic analysis and budgetary cost estimate (±30%); upon completion, perform a sensitivity study of power generation with a post-combustion carbon capture system

* *Factsheet last updated November 2014*

- Develop innovative solvent compositions to reduce the overall cost of carbon capture and storage (CCS) in three steps: (1) establish a performance matrix for solvent formulation and evaluation, (2) formulate the solvent to balance kinetics and thermodynamics, and (3) conduct evaluations at various levels of scale to determine the solvent's performance capabilities compared to the matrix
- Use rational design for future catalyst generation, building on the success of previous synthesized mimic catalysts to enhance the CO_2 mass transfer rate in concentrated amine solutions used for post-combustion capture, to demonstrate catalyst stability and robustness under conditions conducive to post-combustion carbon capture, and to demonstrate catalyst performance in a capture process using coal-derived flue gas
- Develop high-throughput CO_2 capture membranes, leading to improved plant efficiency and reduced capture costs via the design and synthesis of highly CO_2-permselective polyethylene-glycol-based hybrid membrane materials; develop novel methods based on ultrasonically assisted deposition techniques to fabricate ultrathin composite membranes with unprecedented high CO_2 permeances on commercially attractive support platforms; and demonstrate these developed materials and methods via membrane separation evaluations under industrially relevant coal-derived flue gas conditions
- Investigate the use of carbon xerogel and surface-modified carbon xerogel for the enrichment of carbon-loaded monoethanolamine (MEA) and piperazine species using a new flow-through capacitive deionization cell; investigate also integrated cell components with the use of a dc-dc converter to lower overall energy costs

Recent Progress

The research team completed the conceptual simulation for a 1 million tons/year post-combustion CCS project in Gibson-3 using technology developed by China Huaneng and demonstrated at the Shanghai Shidongkou Power Plant.

Researchers started a demonstration project at Duke Energy's Gibson station, where the current cost of CO_2 capture can be effectively evaluated. Catalyst and solvent development will be used to not only prolong the life of the capture solvent, but also to increase mass transfer into the liquid phase, thereby decreasing the size of the absorber necessary in the capture process. The cyclic carbon loadings of the solvent will also be increased through the use of blended solvents.

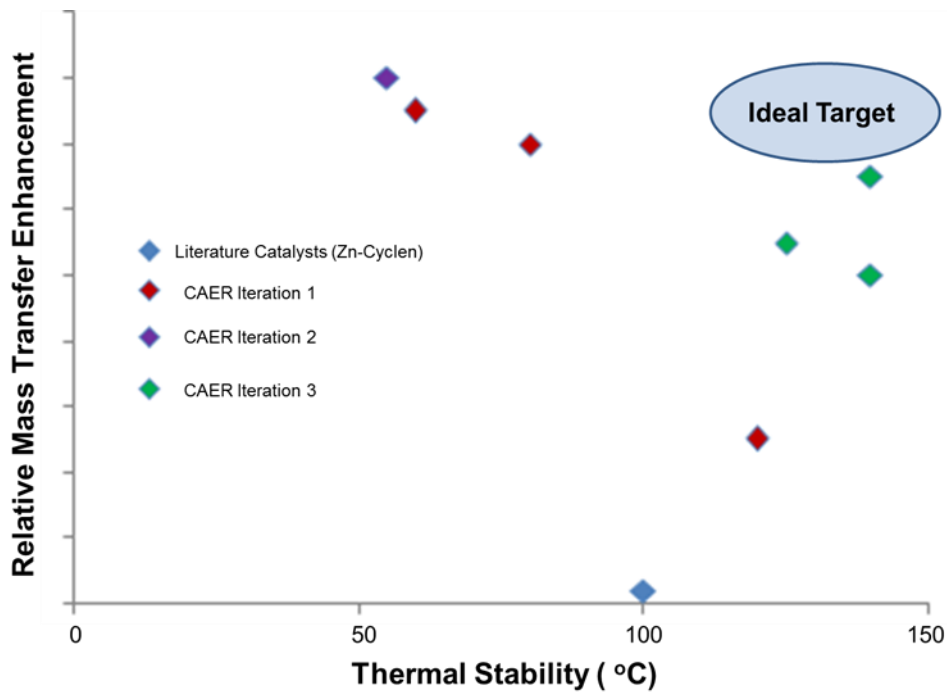

Figure 2. Development progress for robust catalysts towards the CO_2 capture process.

Researchers have continued development on a two-phase (biphasic) solvent for CO_2 capture. Various biphasic solvents have been screened and analyzed. The work has involved the demonstration of the process using a laboratory-scale absorption/desorption column to yield cyclic capacity for various solvent blend compositions. The separation of the CO_2-enriched phase resulted in a low circulation rate and reduced the thermal energy requirements for CO_2 desorption. A $\geq$30% energy reduction in thermal energy by making use of this biphasic solvent has been projected, although process implications for the separation of these phases would need to be addressed for larger-scale implementation.

The U.S. side has been focused on the development and testing of catalysts capable of withstanding the harsh conditions associated with carbon capture. The work has involved demonstration of a new class of catalyst that can tolerate the high temperatures and flue gas impurities derived from NO_x and SO_x gases. Catalyst stability at temperatures up to 140°C and in the presence of flue gas impurities has been established and verified.

A series of candidate catalysts were computationally modeled, guided by previous catalyst results. It was previously concluded, based on computational transition state modeling, that compounds with long Zn–O yet low (<8.5) pKa are needed. Longer Zn–(OH^-) bonds lead to the following:

- Lower Lewis acidity of the metal-ligand complex
- More of a "free" hydroxide (and more nucleophilic)
- Higher pKa for the H_2O deprotonation step

Researchers completed project objectives for the year, including evaluating catalysts under the more realistic conditions observed in a carbon capture process, high temperatures and flue gas impurities. The newly developed catalysts were able to withstand these harsh conditions and maintain their performance in enhancing the overall mass transfer. Further refining the conclusion from last year based on experimental results, the ligand environment and secondary coordination sphere imparted with our catalysts are key to the robustness of this new class of catalysts.

The U.S. side's efforts have been additionally focused on the development of hybrid CO_2 separation membranes with high

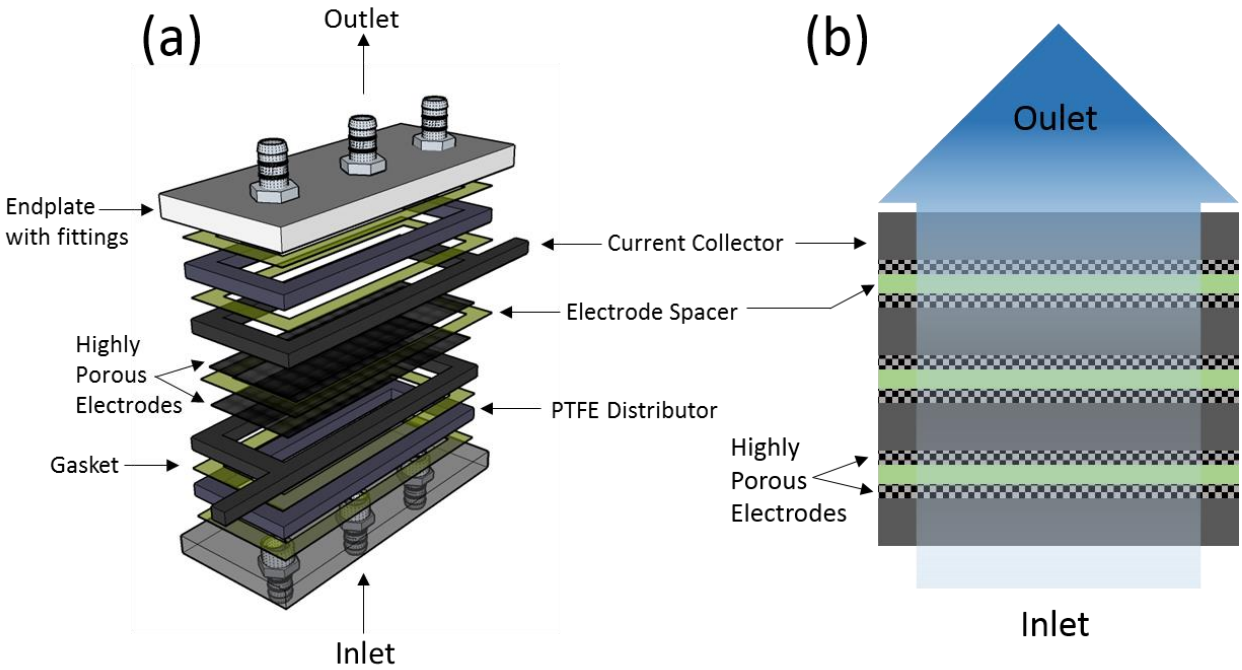

Figure 3. Flow-through capacitive deionization cell for enrichment of carbon-loaded amine solvents. (a) Schematic of the modular cell and (b) illustrative representation of the solution flow path.

permeability and ultra-thin barrier materials enabling high membrane permeance with improved separation efficiency and decreased separation costs. Ultrathin, ionic liquid-based selective layers of these hybrid materials on commercially attractive supports have been developed with selective layers measuring approximately 100 nm. Reduced crystallinity of the active layer was found to dramatically increase the additive retention of the active layer as well as increase the permeance through the membrane. Production of viable fabrication methodologies for the developed membrane materials has also been examined at larger scale to demonstrate the applicability towards larger-scale processes.

Work on capacitive deionization (CDI) for amine solvent enrichment has focused on long-term cycle operation of moderately scaled-up flow-through capacitive deionization cells as well as integration of a new dc-dc converter for lowering the energy costs of the separation process. Enrichment of carbon-loaded piperazine molecules was shown to reach >10% with current cell designs. Further enrichment will be shown for cells with 10X scale-up planned for Year 5. A new dc-dc converter has shown energy recoveries of >20%, reducing the energy cost of this enrichment process. Further reductions will be necessary to decrease the energy cost further for a beneficial impact in the CO_2 capture process. A third-generation converter is already being planned that will reduce losses of various system components with projected energy recoveries of >30%. Year 5 will demonstrate the use of this new converter towards even lower energy costs.

Expected Outcomes

All of the research in this project will be used to show that the energy cost of CO_2 separation from current power plants and the capital cost of the process equipment can be dramatically decreased.

The project will produce optimized design options of competing technology pathways (e.g., advanced solvent) for post-combustion CCUS cost, retrofitability, engineering, and environmental performance. The results from this work will lay the groundwork for decision makers in both China and the United States to understand the potential role of post-combustion retrofits in achieving steep reductions, as well as provide new operational insights into the integration of capture and storage while developing new low-cost, post-combustion capture options.

1 MTons/Year Post Combustion CO_2 Capture at Duke Gibson Station

Joint Project

U.S. Research Team Lead

- **Lawrence Livermore National Laboratory**

U.S. Partners

- **Babcock & Wilcox**
- **Duke Energy**

China Research Team Lead

- **Huaneng Clean Energy Research Institute**

Overview

Researchers performed a pre-engineering studies of the 1 Million Tons/year Post-combustion CO_2 Capture systems, combined with a preliminary Techno-Economic Analysis and Budgetary Cost Estimate (±30%). Efforts focused on the economics of a novel amine-solvent technology for removal of CO_2 from flue gas developed by Huaneng's Clean Energy Research Institute (HNCERI) for implementation by Duke Energy at their Gibson-3 unit in Indiana. Data required for the analysis was provided by HNCERI and by Duke Energy. In addition, the performance of a solvent formulation proposed by Babcock and Wilcox was compared with the previous monoethanolamine (MEA)-based solvents.

Research Objectives

The objective of this task was to perform a Pre-engineering Study of the 1 Million Tons/year Post-combustion CO_2 Capture systems, combined with a preliminary Techno-Economic Analysis and Budgetary Cost Estimate (±30%). Upon completion of these items, a Sensitivity Study of Power Generation with Post-Combustion Carbon Capture System will be performed. The task focused on the two issues below:

- Evaluate the economics of a novel amine-solvent technology for removal of CO_2 from flue gas developed by HNCERI for implementation by Duke Energy at their Gibson-3 unit in Indiana.
- Compare the performance of MEA and MEA-methyldiethanolamine (MDEA)-2-amino-2-methyl-1-propanol (AMP) blend to that of a proprietary Babcock and Wilcox Company (B&W) solvent represented by piperazine (PZ).

Summary of Research Activities

SUMMARY OF TASKS

Over phase 1, research focused on investigating the techno-economic analysis of various carbon capture technologies utilizing a range of amine formulations as power plant retrofits.

- Our approach was to perform a technoeconomic analysis by creating independent process models. Based on the results of those models, we estimated the capital and operating costs of the process to determine the cost of generating electricity while capturing 90% of the CO_2emitted by a fraction of the power unit.
- The amine system we have chosen as our baseline is 30% MEA. Huaneng is developing proprietary novel amine systems that we approximated by a mixture, based on information in a Huaneng patent. We have presented the results for MEA at 30% concentration and the amine mixture at 30% and 35%.
- Beginning in June 2011, the LLNL, Huaneng, and Duke team began to exchange information in order to assess the merits of a post-combustion capture (PCC) retrofit using novel HNCERI technology on a supercritical pulverized coal plant (SC-PC). The technology in question is a liquid solvent capture technology based on mixtures of amines. The three groups agreed to share information, data, and results for the purpose of objective analysis and assessment.
- Using the Gibson-3 analysis as a baseline, we also considered the performance of MEA and MEA-MDEA-AMP blends to that of a proprietary B&W solvent represented by PZ.

MAJOR FINDINGS AND OUTCOMES

For the existing U.S. and Chinese coal-burning fleets, post-combustion capture (PCC) remains a critically important option and viable approach. While companies provide technology for PCC retrofits, the costs and performance of these systems remain largely untested in commercial settings. As such, power generation companies have very few technical or economic data sets on which to base large capital decisions. Moreover, initial estimates suggest the costs will prove prohibitively high in many settings. This analysis provided an independent assessment of solvent performance using realistic power plant operational parameters and carbon capture technologies, and provided an analysis of associated capital and operating costs. We conclude that the Huaneng mixed amine technology represents an improvement over conventional 30% MEA, but that the improvement in operating cost is not only due to reduced heat of regeneration, but also due to lower amine losses from degradation reducing the solvent replacement costs.

Major Achievements

List of Publications

- Jones, D., McVey, T., Friedmann, J., "Location-Specific Technoeconomic Evaluation of a Novel Amine Technology," Energy Procedia 37(2013) 407-416
- D. A. Jones, T. McVey, S. J. Friedmann, Technoeconomic Evaluation of MEA versus Mixed Amines for CO2 Removal at Near-Commercial Scale at Duke Energy Gibson 3 Plant, Lawrence Livermore National Laboratory Technical Report, LLNL-TR-642494

Commercialization

The team estimates that the Huaneng process, especially at 35% concentration, shows modest but definite cost benefits over 30% MEA: with the assessment of the Huaneng process showing up to a 10% operating cost advantage. Capital cost advantages are only seen when using 35% mixed amines, and are slight (3%); however the advantages in energy consumption and solvent degradation are more substantive and are seen for both 30% and 35% mixed amine concentration. We estimate that the cost of CO_2 capture is approximately $60/MWh. Note this does not include the cost of liquefaction and disposal of the CO_2 captured from the plant, although it includes the cost of compression of CO_2 to 150 bar.

Collaboration

Duke Energy provided flue gas compositions and other operational parameters for the Gibson-3 plant as input to the techno-economic analysis.

Huaneng Energy Group's assessment of the solvent composition used in Huaneng's technology is on a patent issued to Xi'an Thermal Power Research Institute, which lists several of the key personnel associated with the Huaneng amine-CO_2 project (e.g. Xu Shishen, Gao Shiwang, Liu Lianbo, amongst others) as inventors. This patent describes compositions of amines to be used as CO_2 capture solvents, with the amine portion being between 50-85% MEA, 20-40% MDEA, and 0-10% of piperazine, with the balance of the amine being a sterically hindered amine (AMP, tertiary-butylaminoethanol [TBE], tertiary- butylaminoethoxyethanol [TBEE] or tertiary-butylaminopropoxyethanol [TBPE]). The patent describes the amines as being used in 10-40% aqueous solution, and with 0.02%-2% of sodium or potassium tetraoxovanadate. Huaneng also provided a description of the carbon capture and sequestration (CCS) system from at its plant at Shidongkou to be used as a basis for modeling that techno-economics of a Gibson-3 retrofit.

The success of the Huaneng-Duke Energy CCS retrofit analysis was largely based on the free exchange of plant design and chemical data.

Conclusions

This effort provides a basis for the analysis of the efficiency and cost of combined power plant-carbon capture systems. It can be used as a basis for techno-economic analysis of proposed plant designs and solvent formulation improvements. Application to other existing and power plant-carbon capture systems, including integrated gasification combined cycle plants, would be a logical extension of this effort.

Development of Catalyst to Enhance CO_2 Capture Kinetics in Scrubber

Collaborative Project

U.S. Research Team Lead

- **University of Kentucky**

U.S. Partners

- **Duke Energy**
- **Babcock & Wilcox**
- **Alstom**

China Research Team Lead

- **Huaneng Group**

Overview

In this thrust area, researchers pursued activities that would lead to a breakthrough in technologies to increase the overall mass transfer within an absorber column to reduce capital cost requirements for carbon capture and sequestration (CCS) systems. The main focus within this thrust area has been the development of homogeneous catalyst additives for amine-based capture solvents. Among the various research tasks that were completed, the most significant were: (1) designed core catalyst structures based on the enzyme Carbonic Anhydrase; (2) tuned the catalyst family to be soluble in concentrated amine-based solvents and stable towards the harsh conditions existed in CCS systems; and (3) successfully verified the effectiveness of these catalysts to enhance mass transfer in packed bed absorption columns utilizing random packing.

Research Objectives

The research objectives over the entire phase I have focused a cost-effective and functional CO_2 hydration catalyst in the concentrated amine solution, included:

- Design CO_2 hydration catalyst to increase scrubber kinetics
- Develop methods to prepare CO_2 hydration catalyst in a cost effective way
- Implement features into the catalysts that impart high solubility and stability in carbon capture solvents

Summary of Research Activities

SUMMARY OF TASKS

Over phase 1, research focused on investigating the design, development, synthesis, and testing of homogeneous CO_2 hydration catalysts as Carbonic Anhydrase mimics to increase the overall mass transfer in the counter-current flow absorption tower equipped with packing material. Fundamental experiments and lab-scale efficacy and verification experiments were conducted under relevant conditions conducive to a coal-derived flue gas capture system.

Further details on research progress include the following:

- Developed a family of catalysts that are soluble in aqueous amines which utilize a facile and cost effective synthetic process (Figure 1).

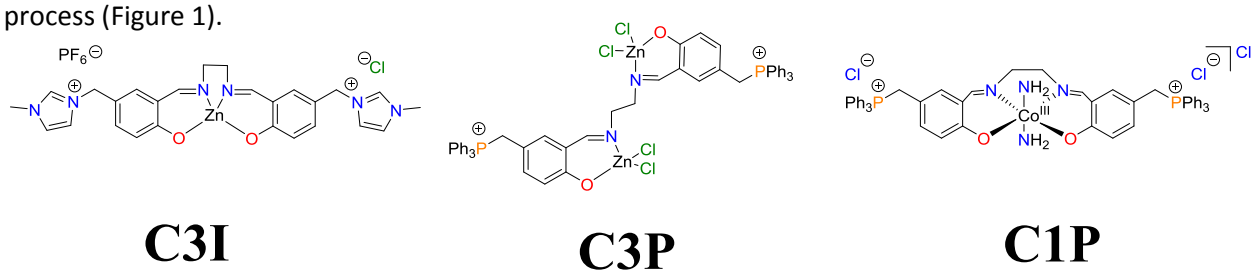

Figure 12: Structures of 1st generation Center for Applied Energy Research (CAER) CO_2 hydration catalysts.

- The catalyst complexes are isolated through simple filtration and require no complicated purification processes
- Carried out efficacy testing of the CAER family of catalysts at the lab-scale under controlled conditions as well as conditions conducive to industrial carbon capture
- Achieved enhancements of up to 40% in overall mass transfer improvements with the addition of CAER catalysts (Figure 2).
- Performed stability testing towards flue gas impurities such as NO_x and SO_x gasses and their corresponding byproducts in capture solutions.
  - The CAER family of catalysts was found to be robust towards flue gas impurities with no loss in activity observed.
- Thermal stability testing of the first generation of CAER catalysts showed that these complexes were not stable at elevated temperatures of over 100°C. An iterative process in collaboration with Lawrence Livermore National Laboratory (LLNL) consisting of catalyst design, computational analysis, catalyst testing, and repeat was performed to produce a series of catalysts that were both stable and highly active in amine-based solvents (Figure 3).

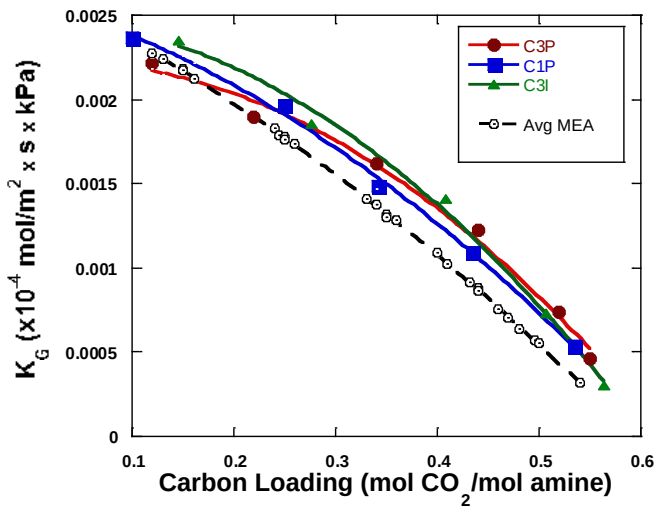

Figure 13: (a) Overall mass transfer coefficients vs. CO2 loading of 30 wt% MEA (black line) and 30 wt% MEA containing with 2.3 g/L C3P (blue line), C3I (green line), or C1P (orange line) obtained using the wetted-wall column set-up at 40°C.

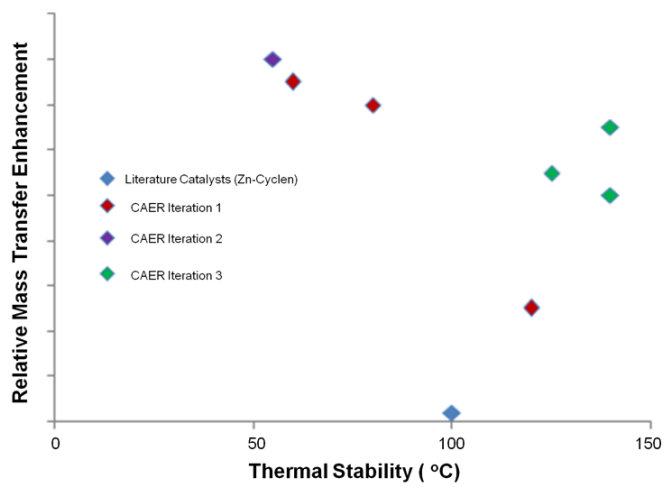

Figure 14: Results and success of the CAER/LLNL iterative process for catalyst design and development to produce active and stable catalysts.

MAJOR FINDINGS AND OUTCOMES

The ground breaking enhancement to overall mass transfer, as demonstrated by the unique and novel CAER CO_2 hydration catalysts will allow for a wider selection of solvents to be utilized. Typically, solvent kinetics dominated the selection criteria which excluded solvents that may have beneficial properties such as thermal and oxidative stability, and lower regeneration energy. With the inclusion of more solvent options, carbon capture systems can be subjected to a more rigorous tuning process to best fit the geographic location and needs.

The CAER catalysts have been shown to increase the overall mass transfer of amine-based solvents by up to 40% which would translate into a ~10% reduction in capital cost of the absorber tower. This is accomplished with transition metal complexes that utilize non-toxic metals that are readily available and cost-effective.

Major Achievements

IP Disclosures

- Joseph E Remias, Cameron A Lippert, Kunlei Liu, Susan Anne Odom, Rachael Ann Burrows, "Catalysts and methods of increasing mass transfer rate of acid gas scrubbing solvents" US 9,266,102.
- Cameron A Lippert, Kunlei Liu, Christine Marie Brandewie, Joseph Eugene Remias, Moushumi Sarma, "Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents" *Patent Pending* US 2014/0,294,705.
- Cameron Lippert, Leland Widger, Moushumi Sarma, Kunlei Liu, "Method of Development and Us of Catalyst-Functionalized Catalytic Particles to Increase the Mass Transfer Rate of Solvents Used in Acid Gas Cleanup" *Patent Pending*, US 62/294,663.

- Cameron Lippert, Leland Widger, Kunlei Liu, "CO_2 Mass Transfer Enhancement of Aqueous Amine Solvents by Particle Additives" *Patent Pending,* US 62/290,293.
- Joseph E Remias, Cameron A Lippert, Kunlei Liu, "Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents" *Patent Pending,* 2015/0,196,875.

Conferences

- Cameron A. Lippert; Deepshikha Gupta; John P. Selegue; Joseph E. Remias; and Kunlei Liu, "Homogenous Catalyst Development for Catalytic Enhancement of CO_2 Capture in Aqueous Solvents", Gordon Research Conference: Catalysis, Colby-Sawyer College, New London, NH, June 25-28, 2012.
- Cameron A. Lippert; Deepshikha Gupta; John P. Selegue; Joseph E. Remias; and Kunlei Liu, "Homogenous Catalyst Development for Catalytic Enhancement of CO_2 Capture in Aqueous Solvents", CERC Technical meeting, Oakland, CA, Jan 7-8, 2013.
- "CO_2 Absorption Enhancement Using Homogenous Catalysts" Korea 4th International Conference on CCS, Jeju, South Korea, 2014.
- "CO_2 Absorption Enhancement Using Homogenous Catalysts" US-China CERC Annual Review Meeting, Hangzhou, China, 2014.

List of Publications

- Rachael A Kelsey, David A Miller, Sean R Parkin, Kun Liu, Joe E Remias, Yue Yang, Felice C Lightstone, Kunlei Liu, Cameron A Lippert, Susan A Odom, "Carbonic anhydrase mimics for enhanced CO 2 absorption in an amine-based capture solvent" *Dalton Trans.* 2016, 45, 324-333.
- Cameron A Lippert, Kun Liu, Moushumi Sarma, Sean R Parkin, Joseph E Remias, Christine M Brandewie, Susan A Odom, Kunlei Liu, "Improving carbon capture from power plant emissions with zinc-and cobalt-based catalysts" *Catal. Sci. Tech.*, 2014**,** 4, 10, 3620-3625.
- Cameron Lippert, Leeland Widger, Moushumi Sarma, and Kunlei Liu "Catalyst Development for Rate Enhanced Acid Gas (CO_2) Scrubbing" *Energy Procedia,* 2014**,** 63, 273-278.

Additional Funding

- Received additional funding from DOE to pursue catalyst candidate testing on CAER's 0.1 MWth bench-scale post-combustion CO_2 capture unit.

Commercialization

The research performed will improve the kinetics within the scrubber tower that could lead to a smaller tower being utilized and thereby reduce the capital cost required for CCS system fabrication. The catalyst testing resulted in up to 40% enhancement in overall mass transfer and increase the potential for the commercialization of amine-based solvents for carbon capture.

Air Liquide has expressed interest in examining these catalysts for natural gas sweetening and CO_2 removal from coal derived syngas.

Conclusions

There is still significant opportunity to increase mass transfer within carbon capture systems and further reduce capital costs. The research team will continue to explore innovative methods to improve process kinetics through the utilization of chemical additives. This research project will not be continued in CERC Phase II.

Post CO_2 Scrubber Solvent Enrichment

Collaborative Project

U.S. Research Team Lead

- **University of Kentucky**

U.S. Partners

- **Duke Energy**
- **Alstom Power**
- **Babcock & Wilcox**

China Research Team Lead

- **Huaneng Clean Energy Research Institute**

Overview

In this thrust area, processes to increase the energy efficiency of a post combustion carbon capture process were investigated including capacitive enrichment techniques and phase-changing solvents, and understanding second generation solvent impacts on process integration and construction materials. Prior to the stripping column in a conventional carbon capture system, a capacitive deionization unit was proposed and demonstrated to enrich process solutions with carbon dioxide-loaded amine molecules. In this manner, the stripping energy required to regenerate the process solution could be limited as the carbon dioxide to water ratio at the top of stripper would be enhanced. Materials developments were used to synthesize carbon electrodes capable of higher enrichment capacities and more stable separations. Carbon electrodes were then used in demonstrations cells to show enrichment of actual carbon dioxide-loaded amine solutions and found to be stable with advanced carbon electrodes developed through this project.

Research Objectives

In this task, advancements to electrode materials and process integration for capacitive deionization (CDI) were shown in an effort to achieve commercially relevant enrichment of carbon-loaded amine molecules for post combustion CO_2 capture operations. New, stable, and high efficiency process operations were discovered and implemented, and integration of cell components was shown to decrease the energy cost of the enrichment. A breakdown of each year's tasks/achievements is shown below.

Objectives for phase I included:

- Developed porous carbon xerogel electrodes for fast-rate adsorption/desorption of carbon dioxide-loaded amine molecules (year 1)
- Modified the surface chemistry of the carbon xerogel electrodes to enhance the adsorption efficiency of the process, limiting device sizes (year 2)
- An advanced process was developed, called inverted capacitive deionization (i-CDI), with significantly increased performance stability and a greater than 500% improvement in separation/enrichment stability during a 600-hr operation run (year 3)
- Examination and scale-up of i-CDI process (>100 g of carbon electrodes) towards adsorption/enrichment of carbon-loaded piperazine (amine) molecules with separation stability (year 4)
- Process integration and energy recovery operations shown for relevant process energy enhancements, greater than 40% energy recovery achieved (year 5)

Summary of Research Activities

SUMMARY OF TASKS

Over phase 1, research in Theme 4.5 has focused on the enrichment of carbon loaded amine molecules in conventional liquid amine post combustion carbon dioxide capture operations. Specifically, on the U.S. side of the project, focus was

directed towards developing advanced carbon electrodes for a capacitive deionization (CDI)/enrichment cell that could achieve enhanced ion adsorption including protonated amine and carbon species prior to the stripping column in a capture operation while maintaining separation or enrichment lifetimes for commercial relevance.

In year one of the project, carbon xerogel electrodes were identified and developed that contained a highly conductive, porous network of mesoporous adsorption sites for fast-rate adsorption/desorption of amine molecules. These electrodes were synthesized at the University of Kentucky (UKy) using a relatively simple polycondensation process and limited process steps or expensive materials. Carbon porosities were modified through the synthesis process with mesoporosity being targeted and optimized during the synthesis for high adsorption/enrichment rate of carbon-loaded amine molecules.

In year two of the project, it was found that adsorption/enrichment efficiencies were less than 40% due to carbon surface chemistry properties at the cathode (negative electrode possessing a negative location for its potential of zero charge) in the cell stack. This discovery required modification of the functional groups of the carbon electrodes to alleviate the inefficiency caused by the material surface charge (e.g. potential of zero charge) on the carbon surface. Materials enhancements were undertaken to modify the carbon surface chemistry and improve enrichment efficiencies to >70%.

Once high efficiencies were achieved, in year three of the project, process lifetimes were examined and found to be prohibitively short for commercial relevance. A new inverted capacitive deionization (i-CDI) process was developed using unique carbon surface chemistries and process operations, which enhanced the performance stability by >500%. The i-CDI process was subsequently demonstrated using the previously synthesized carbon xerogel electrodes as well as commercially available carbon cloth electrodes.

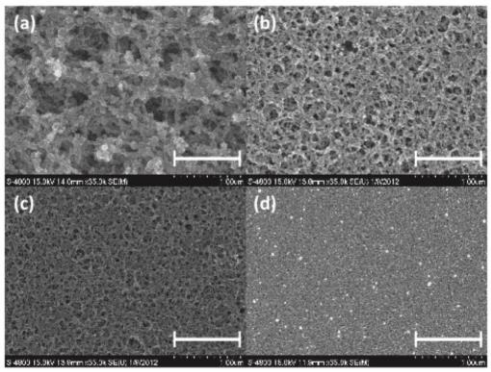

Figure 15: SEM images of external pore size for (a) 37 wt% resorcinol-formaldehyde (RF), (b) 40 wt% RF, (c) 45 wt% RF, and (d) 50 wt% RF. External pore size is a function of the initial RF concentration with the pore size decreasing as the RF weight percent increases. Size bar in the figure is 1 µm.

In year four of the project, this i-CDI process was demonstrated for use with carbon-loaded piperazine (amine) solutions. Initial scale-up operations were undertaken, and the newly developed process was found to be stable in a scaled-up (>100 g) separation cell.

In year five of the project, to enhance the energy efficiency of the process further, process integration activities were carried out using parallel i-CDI cell stacks and a newly UKy-developed dc-dc converter. Through integration of i-CDI cell stacks and developing/implementing a Cuk dc-dc converter, the energy released during discharging or enrichment could be used in a parallel i-CDI cell stack for adsorption of amine molecules, thereby decreasing external power demands. Energy recovery between charging/discharging cell stacks of >40% was achieved, substantially decreasing the energy cost of the separation/enrichment process.

Finally, process assessments were evaluated through this work and target applications identified. For the as-developed i-CDI process, it was found that its highest efficiencies were produced in lower concentration salt streams. For post-combustion carbon dioxide capture, i-CDI would be most competitive with existing separation technologies when used for the enrichment of amine molecules in the water wash section installed at the top of the absorption column or in enhanced water recovery operations as part of carbon dioxide sequestration activities, which will be investigated in the second phase of work.

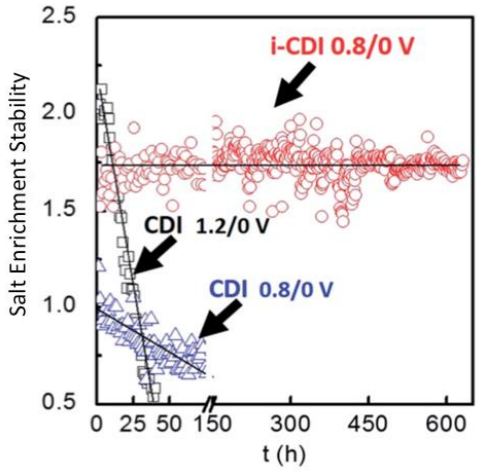

Figure 16: Enhanced stability by the i-CDI system employed with a carbon xerogel (CX) cathode and a silica-functionalized CX anode.

MAJOR FINDINGS AND OUTCOMES

Capacitive deionization (CDI) has long been touted as an energy-efficient separation technology that could be used for many separation/enrichment activities. However, CDI has suffered in prior commercialization efforts due to carbon electrode inefficiencies and short performance lifetimes of less than one month. Through the work in this project, advanced carbon electrodes were developed with exceptionally high efficiencies in comparison to previously demonstrated electrodes. Most importantly, these electrodes were used in the development of a new separation process called inverted capacitive deionization (i-CDI) that shows dramatically longer lifetimes,

making this long-standing efficient technology usable at commercial scales. The use of this technology for a variety of desalination activities, including that for post combustion carbon capture, will have large effects on greenhouse gas emissions.

Major Achievements

List of Publications

- "Power Plant Wastewater Cleanup through Capacitive Deionization" J. Landon, J. K. Neathery, K. Liu. ECS Trans., 2013, 45 (17), 33-42. http://dx.doi.org/10.1149/04517.0033ecst
- "Energy Recovery in Parallel Capacitive Deionization Operations" J. Landon, X. Gao, J. K. Neathery, K. Liu, ECS Trans., 2013, 53, 235-243. http://dx.doi.org/10.1149/05330.0235ecst
- "Investigation of HNO_3-Treated Carbon Xerogels for Capacitive Deionization Applications" X. Gao, J. Landon, J. K. Neathery, K. Liu, ECS Trans., 2013, 53, 219-233. http://dx.doi.org/10.1149/05330.0219ecst
- "Membrane Assisted Capacitive Deionization with Binder-Free Carbon Xerogel Electrodes" A. Omosebi, X. Gao, J. Landon, K. Liu, ECS Trans., 2014, 61 (21), 9-17. http://dx.doi.org/10.1149/06121.0009ecst
- "Impact of Pore Size Characteristics on the Electrosorption Capacity of Carbon Xerogel Electrodes for Capacitive Deionization" J. Landon, X. Gao, B. Kulengowski, J. K. Neathery, K. Liu. J. Electrochem. Soc., 2012, 159, A1861-A1866. http://dx.doi.org/10.1149/2.007212jes (IF 3.266)
- "Modification of Carbon Xerogel Electrodes for More Efficient Asymmetric Capacitive Deionization" X. Gao, J. Landon, J. K. Neathery, K. Liu, J. Electrochem. Soc., 2013, 160, E106-E112. http://dx.doi.org/10.1149/2.111309jes (IF 3.266)
- "Enhancement of Charge Efficiency for a Capacitive Deionization Cell Using Carbon Xerogel with Modified Potential of Zero Charge" X. Gao, A. Omosebi, J. Landon, K. Liu, Electrochemistry Comm., 2014, 39, 22-25.
- "Asymmetric Electrode Configuration for Enhanced Membrane Capacitive Deionization" A. Omosebi, X. Gao, J. Landon, K. Liu, ACS Appl. Mater. Interfaces, 2014, 6 (15), 12640-12649. http://dx.doi.org/10.1021/am5026209 (IF 6.723)
- "Dependence of the Capacitive Deionization Performance on Potential of Zero Charge Shifting of Carbon Xerogel Electrodes during Long-Term Operation" X. Gao, A. Omosebi, J. Landon, K. Liu, J. Electrochem. Soc., 2014, 161, E159-E166. http://dx.doi.org/10.1149/2.0561412jes (IF 3.266)
- "Continuous Operation of Membrane Capacitive Deionization Cells Assembled with Dissimilar Potential of Zero Charge Electrode Pairs" A. Omosebi, X. Gao, J. Rentschler, J. Landon, K. Liu, J. Colloid Interface Sci., 2015, 446, 344-350. http://dx.doi.org/10.1016/j.jcis.2014.11.013 (IF 3.368)
- "Surface Charge Enhanced Carbon Electrodes for Stable and Efficient Capacitive Deionization Using Inverted Adsorption-Desorption Behavior" X. Gao, A. Omosebi, J. Landon, K. Liu, Energy Environ. Sci., 2015, 8 (3), 897-909. http://dx.doi.org/10.1039/C4EE03172E (IF 20.523)
- "Enhanced Salt Removal in an Inverted Capacitive Deionization Cell Using Amine Modified Microporous Carbon Cathodes" X. Gao, A. Omosebi, J. Landon, K. Liu, Envir. Sci. & Tech., accepted. http://dx.doi.org/10.1021/acs.est.5b02320 (IF 5.330).
- "Complementary Surface Charge for Enhanced Capacitive Deionization" X. Gao, S. Porada, A. Omosebi, K. Liu, P. M. Biesheuvel, J. Landon*, Water Research, 2016, 92, X-XX. http://dx.doi.org/10.1016/j.watres.2016.01.048 (IF 5.323)

Additional Funding

- Received additional funding from the state of Wyoming to pursue enhanced water recovery research from CO_2 sequestration operations using advanced carbon electrodes

Commercialization

In phase 1, multiple patents (3) were filed concerning the surface-modified carbon electrodes and process developments around the i-CDI separation cells. Demonstration of this technology at larger scales, such as the work planned in phase 2, will lead towards further potential adoption of the technology by larger separation and water treatment companies.

Collaboration

The U.S. industry collaborators on this project provided consulting expertise and guidance towards advancement of the technology for commercial relevance. Discussions with industry collaborators such as Duke Energy and Alstom took place at periodic meetings in both China (Hangzhou 2014) and the U.S. (Wyoming in 2013 and 2015) as well as other periodic project updates.

Over the course of the phase 1 work, the team worked closely with the Huaneng-led Chinese team, in particular, Jinyi Wang at Huaneng Clean Energy Research Institute, towards the development of advanced enrichment operations for post combustion carbon dioxide capture processes. This work included investigations towards precipitating or phase change solvents as well as the capacitive deionization process mentioned previously. Meetings were conducted both in the U.S. and in China, including Wyoming in 2013 and 2015 and Hangzhou in 2014. Process developments were evaluated based on cost, effectiveness, and relevance.

Conclusions

The work carried out in phase 1 of this project has demonstrated that the i-CDI process is highly capable and efficient for salt separations with particular applications in the water wash section installed at the top of an absorber column in conventional post combustion carbon capture operations or in enhanced water recovery (EWR) efforts during CO_2 sequestration.

Oxy-Combustion CO_2 Capture*

U.S. Research Team Lead

- Washington University in St. Louis (acting team lead)
- Babcock & Wilcox Power Generation Group, Inc.

U.S. Partners

- West Virginia University
- Lawrence Livermore National Laboratory
- National Energy Technology Laboratory

China Research Team Lead

- Huazhong University of Science and Technology

China Partners

- Tsinghua University
- Research Center for Clean Energy and Power, Chinese Academy of Sciences

Research Objective

Researchers from the U.S.–China Advanced Coal Technology Consortium (led by the Huazhong University of Science and Technology [HUST] in China and by Babcock & Wilcox [B&W] and Washington University in St. Louis [WUSTL] in the United States) will collect fundamental and pilot-scale data associated with various oxy-combustion conditions and conduct feasibility and economic analysis on the commercial-scale deployment of the technology for CO_2 capture. The objectives for Theme 5 activities are defined as follows:

- Determine combustion and emission characteristics of indigenous Chinese and U.S. coals of different ranks under oxy-combustion conditions
- Evaluate and optimize pilot-scale oxy-combustion technology
- Develop a computational fluid dynamics (CFD) and process model for oxy-combustion
- Enable knowledge sharing on the feasibility study of the large-scale demonstration

Technical Approach

With experience from previous U.S. work, along with the development of new research pilots in China, an opportunity exists to accelerate the path to commercialization and broaden the application across regions and fuel types. The primary approach focuses on expanding the experience of oxy-combustion into broader applications in the United States and China. The technical approach comprises five main activities:

Fuel characterization and hazardous air pollution emission study under oxy-fuel conditions

- Conduct analysis of representative samples of different ranks of Chinese and U.S. coals
- Conduct experiments on characteristics of coal pyrolysis, ignition, combustion, burn off, dust stratification, slagging, and deposition in bench-scale facilities. Also, conduct tests on NO_x formation and destruction, PM2.5 emission, and control
- Develop and implement reaction chemistry sub-models on combustion and NO_x formation under oxy-combustion conditions to provide a tool for burner design and oxygen injection optimization (HUST's Furnace Model [FURN]) and B&W's Combustion Model [COMO])

Pilot-scale oxy-fuel combustion evaluation and optimization

- Carry out pilot-scale tests in research facilities at B&W and HUST using selected Chinese and U.S. coals
- Configure the research facilities at B&W and HUST for the optimum oxy-combustion flue gas recycling process (e.g., warm-recycle, cool-recycle, or cold-recycle) using a new burner design
- Collect performance data on combustion, heat transfer, furnace exit gas temperature, and emissions over a wide range of practical operating conditions

† *Factsheet last updated November 2014*

- Select the most promising design, based on modeling predictions and performance criteria for further demonstration

Steady-state and dynamic process modeling simulations

- Compare Aspen Plus static predictions with pilot-scale data
- Use Aspen Plus Dynamics to simulate transient oxy-combustion processes
- Validate and tune the dynamic process model toward developing a control strategy for start-up, shutdown, modulations, and unit trips (e.g., boiler, air separation unit, and compression and purification unit)

Feasibility study for large-scale deployment

- Facilitate information exchange on policy, investment, and technical issues to conduct a feasibility study of a reference wall-fired pulverized-coal-burning unit for oxy-combustion
- Perform unit and process concept reviews of the air separation unit, boiler island, compression and purification unit, and the balance of plant

Evaluation of novel staged oxy-combustion concept

- Conduct small pilot testing (100–500 kW) under reduced flue gas recycle (increased oxygen concentration) conditions
- Obtain experimental data set for CFD model validation
- Study fly ash and deposition characteristics

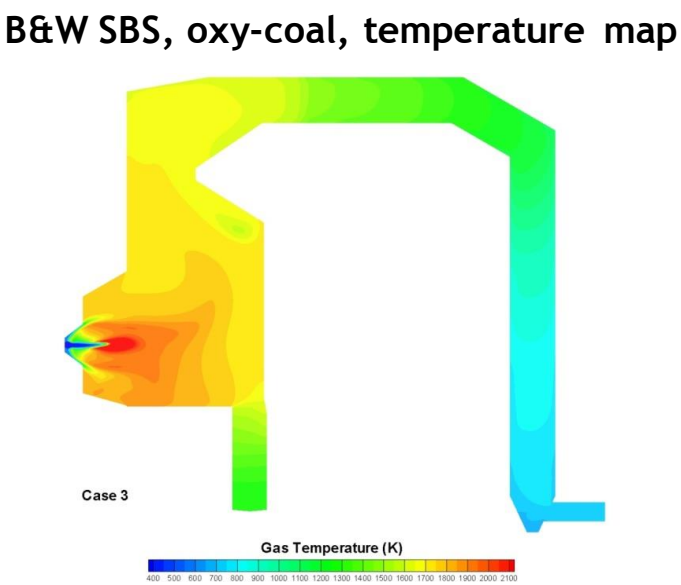

Figure 1. B&W small-boiler simulator oxy-coal temperature map.

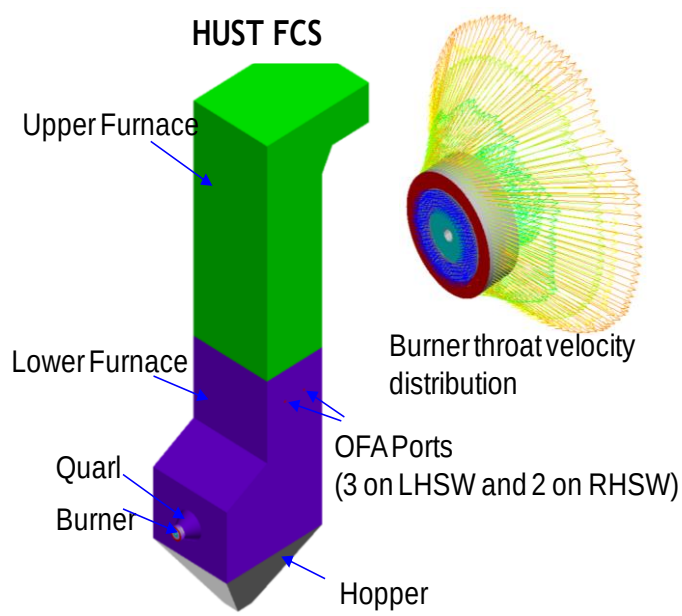

Figure 2. HUST full chain system.

Recent Progress

The gas reaction mechanism for oxy-fuel combustion with dry and wet recycle have been developed, and the predictions of gas temperature and composition are more accurate. Based on spectral line-based, a new WSGG model have been developed, which has obvious advantages in non-isothermal and non-homogeneous gas mixture. Predictions of temperature from the HUST CFD model have been compared to experimental data, and good agreement was found.

The characteristics of ash deposits in a CFB were experimentally determined. Oxy-fuel combustion had an obvious influence on the deposition rate, fine particle emissions and the content of S, K, and Na in ash deposits. The effects of sorbent injection (limestone) on deposits were also studied.

Combustion experiments at WUSTL were performed under conditions of increased oxygen concentration. Measurements of temperature, wall heat flux and NOx were taken. This data is being compared against predictions from ANSYS FLUENT CFD model. Model results indicate that heat flux can be controlled in high-oxygen environments by manipulating flame shape and swirl.

An ASPEN process model of HUST's full chain system (FCS) was developed and an exergy-based optimization method was performed to determine optimal control strategy for flue gas recycle.

Figure 3. China and U.S. research pilots.

Expected Outcomes

This project will lead to cost and performance improvements that are rooted in fundamental science from testing in the laboratory and the field. The use of computer simulation and modeling will allow for greater progress on future demonstrations by reducing risk and optimizing both design and critical areas that require large-scale validation. Ultimately, the economic and environmental potential of oxy-firing combustion will be attributable to a wider range of solid fuels and at a commercially viable scale. The use of the computer models, once validated at large-scale commercial projects, will reduce the risk of deployment and increase the speed of deployment for a wide variety of world coals that normally present additional challenges. These small-scale pilots and the computer models will then become a valuable tool for faster deployment of cutting-edge technology in a long-lived, capital-intensive market space.

Evaluate Novel Staged Oxy-Combustion Concept

Collaborative Project

U.S. Research Team Lead

- **Washington University in St. Louis (WUSTL)**

Overview

In this subtask, the project team evaluated a novel staged oxy-combustion concept. The aim of the work conducted under the CERC program is to evaluate a fuel-staging approach for oxy-combustion of coal, as a means to reduce flue gas recycle and cost of electricity. This subtask is carried out by Washington University (WUSTL), which began its participation in the US-China CERC-ACTC after invitation in 2013. The research reported here is supported by the Consortium for Clean Coal Utilization (CCCU) at WUSTL and its sponsors Arch Coal, Peabody Energy and Ameren.

Research Objectives

- Conduct small pilot testing (100-500 kW) under reduced flue gas recycle (increased oxygen concentration) conditions
- Obtain experimental data set for Computational Fluid Dynamic (CFD) model validation
- Study fly ash and deposition characteristics

Summary of Research Activities

SUMMARY OF TASKS

An experimental test campaign was undertaken at the Advanced Coal & Energy Research Facility, which houses a 1 MWt oxy-combustion test furnace with a swirl-stabilized burner (Figure 1). The aim of the testing was to characterize the oxy-combustion of coal under conditions of decreased flue gas recirculation or, similarly, increased oxygen concentration, in order to simulate conditions in the early stages of the staged combustion process. In these early stages, there is a large excess of O_2 that acts as a dilution gas to reduce the temperature of combustion products. Combustion tests were conducted utilizing oxygen-enriched air, up to 50%v O_2. Measurements of wall radiative heat flux were obtained. Gas temperature measurements were carried out using a suction pyrometer, and gaseous concentration profile (O_2, CO_2, CO, NOx) were obtained by gas sampling. These measurements were compared against predictions from the CFD combustion model (Figure 2), and reasonably good agreement was obtained.

Figure 1: 1 MWt Oxy-combustion furnace at the Advanced Coal & Energy Research Facility (ACERF)

An oxygen concentration of 50% in the secondary oxidant resulted in an increase in peak radiative heat flux of 37%, when compared to air-firing. In spite of the increased local flame temperature in the combustion zone, it was found that the post-flame temperature remained largely unaffected by the oxygen enrichment, which was predicted. At 50% O_2, however, the resulting flame was very short, which limited our ability to accurately measure temperature and heat flux profiles. More importantly, CFD modeling suggested that a long flame was necessary in order to achieve a distributed heat release while maintaining optimal radiant heat flux levels under conditions of high oxygen concentration. To achieve the desired flame shape, a new burner and chamber design was required.

The team, guided by CFD simulation, designed and constructed a new 1 atm, 30 kWt test furnace and burner (Figure 3). This furnace was specifically designed for high-temperature combustion of coal in pure oxygen. The burner was designed to operate with only axial flow (no swirl), and achieve a stable jet flame. This no-swirl design also acted to reduce ash deposition and slagging on the furnace walls. This unique down-fired furnace was made long and narrow to mimic the

high aspect ratio typical of pressure vessels and to achieve a sufficiently high gas velocity such that the effects of buoyancy were minimal.

Stable and safe combustion of both pulverized coal and gaseous fuels was demonstrated in atmospheres of 100% O_2. Despite the fact that combustion in pure O_2 resulted in local regions of very high combustion temperature, the furnace and burner design proved successful in preventing flame impingement on the wall and wall overheating. Furthermore, no measureable ash deposition on the furnace walls was detected while operating over a period of several hours. The knowledge gained from the design and operation of this facility has been implemented in the construction of a new pressurized oxy-combustion test furnace which will be operating in 2016. Meanwhile, this 30 kWt facility will continue to be a valuable asset for the study of particle formation and deposition under conditions of very high flame temperature.

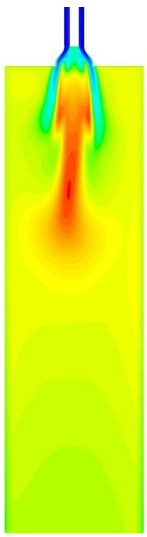

Figure 2: False-color temperature distribution during pulverized coal combustion, as predicted by CFD modeling.

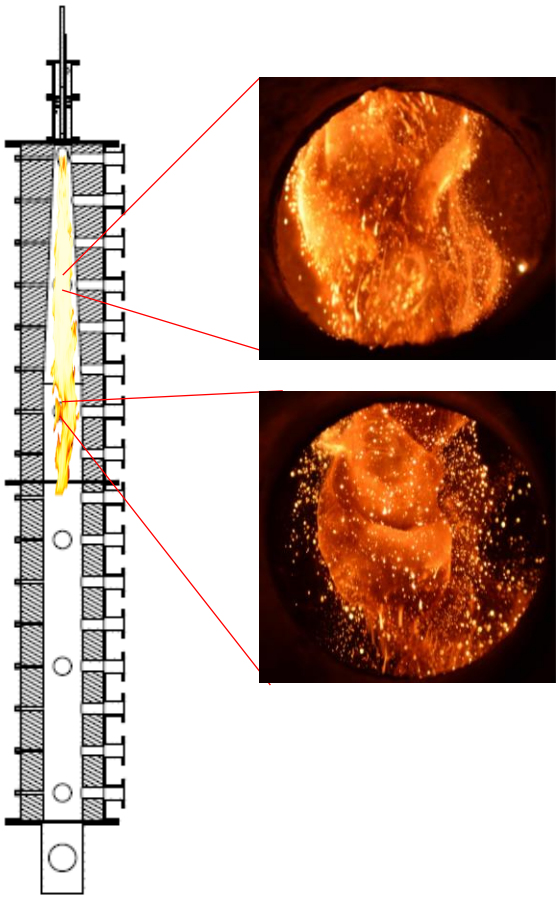

Figure 3: Schematic of 30 kWt test furnace. Images obtained from high-speed camera show combustion of pulverized coal (with CO_2 carrier gas) in atmosphere of 100% oxygen.

Major Achievements

Workshops

- Dhungel, B, Xia F, Kumfer BM, Axelbaum RL. Investigation of oxygen enriched combustion for application to a novel fuel-staged pressurized oxy-combustion (SPOC) process. The 39th International Technical Conference on Clean Coal & Fuel Systems , Clearwater, FL, Jun. 1-5, 2014.
- Kumfer, B. M. Evaluation of Staged Oxyfuel Combustion for CO_2 Capture. 2015 Clean Coal Technology Research Symposium, Laramie, WY, Aug 20, 2015.
- Gopan A, Yang Z, Adeosun A, Kumfer BM, Axelbaum RL, Effect of stoichiometric ratio and oxygen concentration on heat flux profiles in oxy-coal combustion. 9th U. S. National Combustion Meeting, Cincinnati, Ohio, 2015.

Collaboration

WUSTL was pleased to host Prof. Chuguang Zheng, Zhaohui Liu and Tianhua Wu from Huazhong University of Science & Technology (HUST) during a visit to St. Louis in 2013. The research interests and capabilities of the two universities were discussed, and areas of potential collaboration were identified. A second group of researchers from HUST visited WUSTL in 2014, and gave a series of technical presentations to students and faculty on their coal and oxy-combustion research efforts.

WUSTL also hosted a visiting professor from HUST in 2014. Dr. Chun Lou has been collaborating with Prof. Richard Axelbaum and Ben Kumfer to develop camera-based diagnostics for the measurement of temperature, soot fraction, and radiation under oxy-combustion conditions. A joint abstract was submitted to the Spring Technical Meeting of the Central States Section of The Combustion Institute. Kumfer also visited HUST for one week in 2015 to conduct joint research with Dr. Chun Lou at the State Key Laboratory for Coal Combustion. Experiments were performed to investigate changes in soot fraction and emission spectra of gaseous laminar flames under various oxy-combustion conditions. It was demonstrated that soot fraction may be drastically altered, depending upon how oxygen and CO_2 are injected. It was also shown that high-temperature flames with reduced flue gas recycle may be created without increased soot formation. A joint paper is in preparation.

Prof. Axelbaum has been working in a collaboration with Prof. Shuiqing Li at Tsinghua University, who is an expert in the field of ash deposition, to develop models and conduct experiments that will provide a better understanding of the behavior of ash deposition in various oxy-combustion environments. Axelbaum has hosted two PhD students from Prof. Li's group, and several joint papers or abstracts have been produced. A unique two-stage Hencken-style laboratory burner was co-developed, which will provide a valuable tool for the detailed study of coal particle ignition, char formation and burnout, and ash particle formation under various oxy-combustion conditions.

Conclusions

Pressurized oxy-combustion holds promise to achieve capture of carbon dioxide at significantly higher efficiency and reduced costs, as compared to first-generation, atmospheric pressure oxy-combustion systems, and meet U.S. Department of Energy (DOE) cost and performance targets for advanced combustion systems. A new facility has been constructed at WUSTL with DOE support, which will allow for testing of oxy-combustion of pulverized coal at a pressure of up to 15 atm. Under Phase II of the CERC program, this facility will be operated over the next several years to obtain critical experimental data needed for model validation and to fill knowledge gaps. Other planned activities include process modeling and Reynolds-Averaged Navier-Stokes (RANS) and Large Eddy Simulation (LES) CFD modeling, in collaboration with Prof. Celik at WVU.

WUSTL will continue to work with collaborators in China from HUST, Tsinghua University, Harbin Institute of Technology, and Southeast University. Together, this team will work to obtain fundamental data on the behavior of coal combustion at elevated pressure in oxy-combustion environments. This data will be useful for advancing the development of many proposed pressurized oxy-combustion (POC) concepts, including fluidized bed combustion, flameless combustion, POC with steam injection, and fuel-staged POC.

CO_2 Sequestration*

U.S. Research Team Lead

- Los Alamos National Laboratory
- University of Wyoming

U.S. Partners

- Lawrence Livermore National Laboratory
- Indiana Geological Survey
- West Virginia University
- Duke Energy
- National Energy Technology Laboratory

China Research Team Lead

- Institute of Rock and Soil Mechanics, Chinese Academy of Sciences

China Partners

- Shaanxi Provincial Institute of Energy Resources
- Yanchang Petroleum Group
- Huaneng Group
- Shenhua Group
- Qinghua University
- China University of Mining and Technology, Beijing
- China University of Mining and Technology, Xuzhou

Research Objective

This theme's research is focused on identifying utilization targets overlying deep saline reservoirs and integrating carbon capture, utilization, and storage. Target basins include the Ordos and Bohai basins, China, and the Rock Springs Uplift and Illinois Basin in the United States. This effort includes the following:

- Characterize targeted geological storage reservoirs in three dimensions, on both regional and site-specific scales, based on all available public geological, geophysical, geochemical, petrophysical, petrographic, and petroleum engineering data. This research is especially concerned with characterizing reservoir and seal heterogeneity, as well as the effects of heterogeneity on CO_2 injectivity and storage capacity assessments
- Develop the scientific, technological, and engineering framework required for CO_2 utilization in the Illinois and Ordos basins via enhanced oil recovery (EOR), shale gas, and enhanced coal bed methane (ECBM). Utilization in the Bohai Basin (Tianjin) includes enhanced water recovery (EWR) and couples to capture at the Huaneng GreenGen IGCC facility. The utilization strategy will include safe, permanent storage of large quantities of anthropogenic CO_2
- Develop simulation technology for CO_2 storage in saline formations
- Research and apply monitoring technology of CO_2 storage in saline formations
- Assess safety and risk of CO_2 storage in saline formations
- Understand system feedbacks, including the impacts of source locations on optimization of storage systems
- Conduct geological characterization at multiple data resolutions

Through combined research on these issues and successful execution of demonstration projects, this effort will improve understanding, provide verification of key technologies for CO_2 storage in saline formations, and provide the scientific evidence to implement large-scale CCS and CCUS in China and the United States.

The project has two primary objectives:

- Build the scientific, technological, and engineering framework necessary for CO_2 utilization through EOR and EWR, and the safe, permanent storage of commercial quantities of anthropogenic CO_2 in geologic formations in both China and the United States
- Assess the safety and risk of CO_2 storage in saline formations

* *Factsheet last updated November 2014*

Technical Approach

In the near term (2014), the team plans to accelerate data collection and move forward with work in Ordos and Bohai Bay basins (China), the Illinois Basin, and the Green River Basin (Rock Springs Uplift) in Wyoming. Both the United States and China are working to determine what data can be released publicly to facilitate collaboration that will allow use of the best algorithms from both China and the United States. The team continues to monitor the progress of developments in the coal-to-liquid industry in the Ordos Basin as sources of lower-cost CO_2 for EOR.

Collaboration at the site scale requires application-dependent cooperation that may or may not involve direct sharing of sensitive data. Sharing executable algorithms will allow teams on either side to create results using the range of tools available to the U.S.–China Clean Energy Research Center (CERC). The team will continue to pursue opportunities to exchange personnel to increase productivity and joint understanding of algorithm implementation.

Both U.S. and Chinese teams continue to develop models for specific sites in their own countries that will support the overall goals of the project without constraints. Specifically, using the University of Wyoming projects as analogs, the team proposes to work closely with research scientists from the Shaanxi Provincial Institute of Energy Resources and Chemical Engineering and Northwest University to assess the anthropogenic CO_2 resources and geological CO_2 storage capacity of the Ordos Basin.

Methods employed in a comprehensive regional storage analysis include coupling impacts related to the reality of multiple sources linked to multiple possible sinks including all relevant sources of uncertainty. Such regional studies allow intelligent development of both capture systems and storage sites based on evolving CO_2 capture goals. Algorithms developed at LANL over the past several years are being driven by detailed data on CO_2 sources, utilization targets, surface features (mountains, rivers, cities, etc.), and estimates of both storage capacity and injectivity for specific reservoirs. We are using the approaches developed in our previous work with new modifications to tackle ECBM/Shale Gas/EOR/Saline CO_2 storage questions associated with the Gibson/southern Indiana region and plan to teach/demonstrate the same techniques to our collaborators from the Chinese Academy of Science and Northwestern University.

Recent Progress

The Yangchang Oil Company has initiated a CO_2 storage and CO_2–EOR project, and injection of CO_2 was successful (Figure 1). Company representatives visited Wyoming to seek assistance with project design (e.g., reservoir heterogeneity characterization, structural and property modeling, injection and production simulation, economic evaluation). The joint project team arranged a joint field trip in the Ordos Basin to study the targeted storage reservoirs and potential sealing strata, and to observe cores in the Yanchang and North China Oil Company core repository. To assist the Yanchang Oil Company with its CO_2–EOR and storage demonstration projects, the team organized a trip to work on the reservoir data at the Yanchang facility in order to continue to build structural and property models.

A visit to Los Alamos National Laboratory in September 2013 by Dr. Bai of the Chinese Academy of Sciences led to data sharing on sources of CO_2 located around the Ordos Basin. This data sharing allowed us to create a source/sink model of

Figure 1. CO_2 injection in the Ordos Basin.

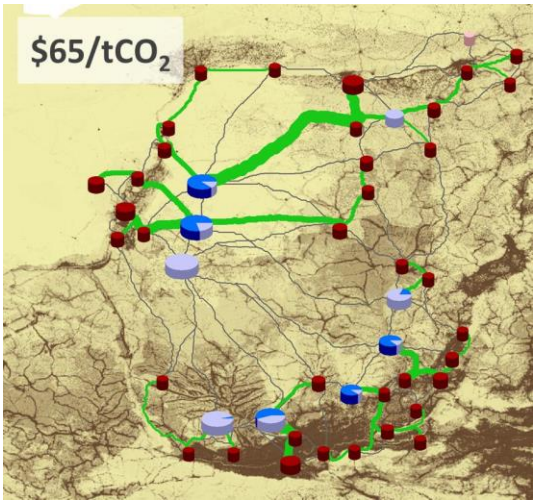

Figure 2. Source-sink matching in the Ordos, China.

what large-scale (50–300 MT/yr) CCS might look like in the future (Figure 2). This work was presented at GHGT-12 in Austin, October 2014. A workshop in May 2014 in Wuhan brought together many of the primary researchers, and progress was made in determining how to proceed with generating regional-scale data from publicly available sources that can be shared between both countries. Additionally, initial work in the Illinois Basin on stacked CO_2 utilization with deeper large saline reservoirs for a range of CO_2 capture (1–15 MT/yr) was presented to Duke Energy, and a report is being generated based on suggestions from the presentation.

Using these models, the team will perform, at facilities in Wyoming, numerical simulations for the targeted reservoir and storage site. Detailed three-dimensional geological, structural, and property models are being constructed for the selected mature oil reservoir (i.e., targeted CO_2 flooding reservoir). Reservoir heterogeneity will be built into these models using outcrop and core observations, well log analyses, seismic interpretations, and Wyoming analogs (Figure 3).

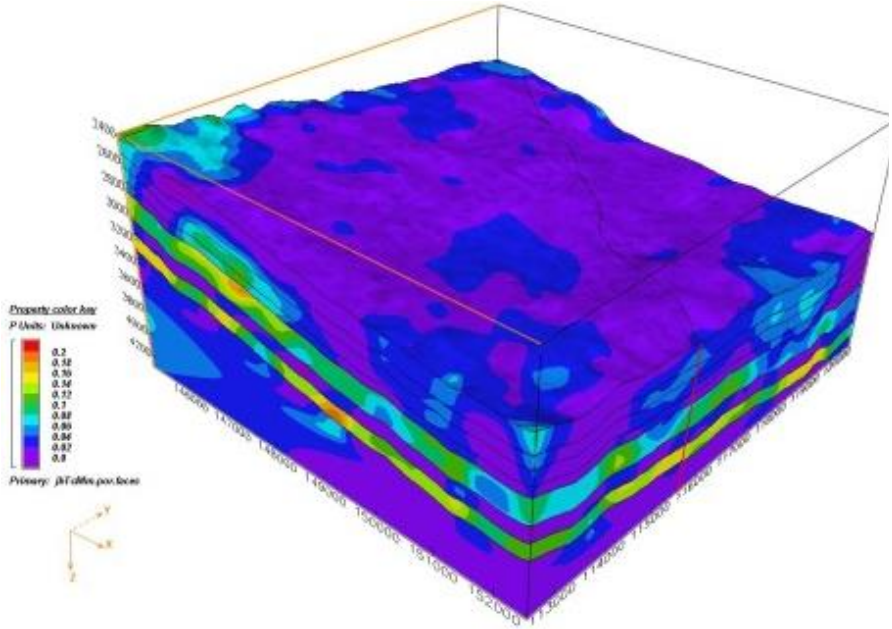

Figure 3. High resolution 3-D seismic data from Wyoming used for capacity and injectivity analysis.

In the last year, the partners from Northwest University, Shaanxi Provincial Institute of Energy Resources and Chemical Engineering, the Yanchang Petroleum Company, the North China Oil Company, the Institute of Rock and Soil Mechanics, China University of Mining and Technology, the University of Wyoming, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, the Indiana Geological Survey, and West Virginia University have accomplished the following tasks:

- Assembled a large set of information regarding the geologic, petrophysical structural/stratigraphic frameworks of the Ordos Basin, Rock Springs Uplift, and Illinois Basin
- Inventoried the distribution of fossil energy and anthropogenic CO2 resources in the Ordos Basin
- Delineated CO2 sources, sinks, and utilization targets in the Illinois and Ordos basins in a presentation to Duke Energy
- Delineated CO2 sources for Wyoming
- Explored the potential of developing CCUS analogs between the Ordos Basin and the Powder River/Green River Basin and Illinois Basin using the latest screening criteria
- Published results from a numerical study of CO2 injectivity, storage capacity, and leakage for the Rock Springs Uplift in Wyoming in the International Journal of Greenhouse Gas Control (impact factor [IF] 5)
- Published results from an analysis of the impacts of CO2 source variability on storage costs in Applied Energy (IF 5)
- Published source sink matching work in the Ordos Basin (Energy Procedia, Figure 2)
- Published a methodology for regional-scale system analysis using data from the southeast United States in Energy & Environmental Science (IF 15, Figure 4); methodology adapted partially from the National Risk Assessment Partnership (NRAP) and applied to the Gibson site to emulate multiphase flow and reactive transport
- Published work on a path forward in the United States for CCUS using high-value chemicals (Energy Procedia)
- Published in Environmental Science and Technology on how utilization and CO2 sources are not well matched (IF 5)
- Developed site prioritization methods and ranked saline storage reservoirs
- Leveraged collaboration between the Yangchang Oil Company and the Theme 6 team to initiate design, construction, and injection at a pilot CO2–EOR project in the Ordos Basin
- Delivered a 70-page pre-feasibility study on EWR coupled to CO_2 capture at the GreenGen facility to the Huaneng Group

Expected Outcomes

The significant opportunity for storage and utilization of CO_2 in the Ordos Basin in China complements opportunities that are being explored in basins in the United States, such as in Wyoming and Illinois. The research team is looking at the Ordos Basin in parallel to this research. The lessons learned will be invaluable to CCS projects, particularly in Rocky Mountain basins; the Majiagou Limestone and Ordos Basin are very similar to the Paleozoic Madison Limestone and the Powder River Basin of Wyoming and Montana.

This work ultimately improves global understanding of how to safely and effectively store CO_2 in saline formations or to use the CO_2 for EOR.

The most important outcomes expected at the end of Year 5 are as follows:

- Jointly developed structural, property, and numerical models (including the heterogeneity of the reservoir/seal system) for the highest-priority geological CO_2 storage reservoirs and sites in the Ordos, Green River, and Illinois basins
- A detailed evaluation of all anthropogenic CO_2 sources and sinks in the Ordos, Green River, and Illinois basins
- Initial optimization strategies for pipeline networks in the same basins considering utilization targets such as EOR, EWR, ECBM, and shale gas co-located with deeper saline storage reservoirs.
- A demonstration project, developed in cooperation with Theme 6 partners, to evaluate the potential of integrated geological CO_2 storage with EOR and/or EWR using CO_2 flooding
- A Phase 2 feasibility study for the GreenGen EWR project in Tianjin, China

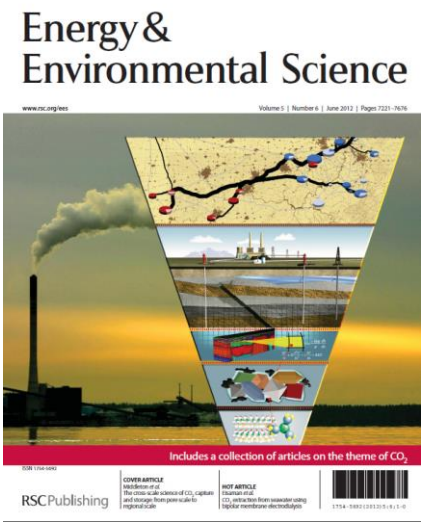

Figure 4. CERC ACTC journal cover on linking CO_2 sources to CO_2 storage reservoirs.

Saline Formation Storage at the Basin Scale

Joint Project

U.S. Research Team Lead

- **University of Wyoming**

China Research Team Lead

- **Shaanxi Provincial Institute of Energy Resources and Chemical Engineering**

China Partners

- **Rock and Soil Mechanic Institute, Chinese Academy of Sciences**
- **Yanchang Petroleum Group Research Institute**

Overview

The U.S. and China are the two largest producers of CO_2 emissions in the world. It is essential for these two countries to collaborate in searching for solutions to climate change through carbon reduction. The IPCC's Fifth Assessment Synthesis Report (2015) reported that most climate models could not meet emission reduction targets without carbon capture, utilization and storage (CCUS). Applying its experiences on geologic CO_2 storage-site characterization projects, the University of Wyoming Carbon Management Institute (UW CMI) team has made substantial achievements in CERC-ACTC Phase I on CCUS. The database generated and lessons learned from the geological CO_2 storage site characterization projects in Wyoming proved invaluable for the cooperation projects conducted during the CERC-ACTC Phase I program. The similar foreland geological structure and saline aquifers in the Wyoming Laramide basins and Shaanxi Ordos Basin provide a unique opportunity for U.S. and Chinese partners to work closely on developing collaborative technologies and techniques for a commercial-scale geological CO_2 storage project. Through Phase I, the UW CMI team has worked closely with partners at the Shaanxi Provincial Institute of Energy Resources and Chemical Engineering (SPIERCE), Northwest University (NWU), Yanchang Petroleum Group (YPG), Institute of Rock and Soil Mechanics of Chinese Academy of Sciences (IRSM), and Huaneng Clean Energy Research Institute (HCERI). The UW CMI team and partners have assembled and analyzed the geologic, geophysical, geochemical, petrophysical, and petrographic data available for the Ordos Basin and Wyoming Laramide basins. The team has applied this data to generate site-specific geological and property models, to conduct numerical CO_2 injection simulations, to evaluate the storage capacities and injectivities of potential saline aquifers in both Wyoming Laramide basins and the Ordos Basin, and assessed the challenges associated with commercial-scale geological CO_2 storage projects for both countries.

Research Objectives

The goal is to build the scientific, technological, and engineering framework necessary for safe, permanent storage of large quantities of anthropogenic CO_2 in the sedimentary basins of the Shaanxi Province and the state of Wyoming by:

- Determining the distribution of potential sealing formations and appropriate geological structure;
- Assessing the potential storage capacity of major saline aquifers in the Ordos Basin and Wyoming Laramide Basins;
- Constructing a 3-D geological model of the storage domain for selected storage sites; and
- Completing performance assessments for a variety of injection/storage scenarios at targeted sites using numerical simulations.

Summary of Research Activities

SUMMARY OF TASKS

The following tasks have been completed during CERC-ACTC Phase I.

- Assessments of available CCUS technologies
- Established a Shaanxi/Wyoming partnership

- Assembly of geologic and geographic data from the Ordos Basin in China and the Rock Springs Uplift in Wyoming
- Assessments of oil, gas, and coal resources in the Ordos Basin and Wyoming basins
- Inventories of anthropogenic CO_2 sources in the Ordos Basin and Wyoming basins
- Established a process for geological CO_2 storage site characterization
- Prioritization of the CO_2 geologic storage capacities of major structures and stratigraphic sections in the Ordos Basin and Wyoming basins
- Generated geologic structure models for the Ordos Basin and the Rock Springs Uplift in Wyoming
- Selection of the most favorable site for a CCUS demonstration project in the Ordos Basin and Wyoming
- Generation of a 3-D computational mesh and conducting CO_2 injection simulations for the Majiagou Formation in the Ordos Basin and the Madison Limestone and Weber Sandstone in the Rock Springs Uplift relative to CCUS
- Determination of the storage capacities of the Ordos Basin and Rock Springs Uplift based on the volumetric approach and numerical simulations
- Summary of results and lessons learned from the CERC Phase I investigations

Geological CO_2 storage capacity assessment in Wyoming

Two geologic structures in southwest Wyoming can store commercial amounts of CO_2 in Paleozoic formations (the Rock Springs Uplift (RSU) and the Moxa Arch). Paleozoic saline aquifers in the RSU and Moxa Arch are the most promising targets for geologic CO_2 sequestration in Wyoming, and probably in any Rocky Mountain basin: foremost among these are the Madison/Bighorn and Tensleep/Weber/ Minnelusa formations (Surdam and Jiao, 2007; Frost et al., 2009). These storage units are overlain by a thick series of sealing lithologies that serve as regional hydrocarbon, CO_2, and helium seals, thus ensuring fluid containment. The targeted carbonate and sandstone saline aquifers lie at depths below all underground sources of drinking water (USDW) and at pressures/temperatures for which CO_2 will be supercritical. Our geological CO_2 storage site characterizations documented porosity and permeability distributions, capillary properties, intraformational and cross-formational flow barrier surfaces, large- and small-scale fluid-flow compartments, potential rock-fluid reaction domains, and large and small fracture elements with respect to variation in reservoir and fluid-flow parameters on a pore to regional scale. The storage capacity assessments suggest that the RSU can store 26 billion tonnes of CO_2, and the Moxa Arch can store 16 billion tonnes of CO_2, capacities that are orders of magnitude greater than the >30 million tonne capacity sites sought by DOE. These capacities are sufficient to store Wyoming's current annual CO_2 emissions of 55 Mt/yr for more than 760 years. These geologic sites are adjacent to several significant sources of anthropogenic CO_2, including PacifiCorp's Jim Bridger power plant (2,200 MW; 15 Mt CO_2 emitted per year), Naughton power plant (700 MW; 6 Mt CO_2 emitted per year), and world largest trona mines (5 Mt CO_2 emitted per year) which together account for approximately 47% of Wyoming's annual CO_2 emissions. In addition, ExxonMobil's gas processing facility on the Moxa Arch produces approximately 10 Mt of CO_2 per year, most of which is sold for enhanced oil recovery, but some of which is vented or disposed of in deep acid gas injection wells.

From these studies, the UW CMI team has shown that the most critical problem with commercial-scale CO_2 storage is the management of the reservoir pressure change resulting from large amount fluid injections. To solve this problem, the team proposes an integrated strategy, where necessary; that includes coupling CO_2 injection with displaced fluid production/water treatment. The results of UW geological CO_2 storage site characterization projects has also shown that the greatest uncertainty in numerically simulating CO_2 sequestration processes and in risk analyses is characterizing geological heterogeneity in three dimensions.

Geological CO_2 storage capacity assessment in the Ordos Basin, Shaanxi

The same approach used for assessing the capacity of potential geological CO_2 storage reservoirs in Wyoming was applied to the Ordos Basin. A Monte Carlo simulation from Goldsim with 10,000 realizations was set up for the Majiagou Formation between depths of 1,000 and 4,000 m in the Shaanbei Slope of the Ordos Basin, China. The probability density of the CO_2 storage capacity of the Majiagou Formation in the Ordos Basin ranges from 60 to 700 Gt, with a mean of 287 GT. Even with a conservative number of 60 Gt of storage capacity, the Majiagou Formation has sufficient storage capacity to accommodate over 300 years of CO_2 emissions generated by the stationary anthropogenic CO_2 emission sources (200 Mt/year reported) in the Ordos Basin.

The Ordos Basin

Successful implementation of geological CO_2 sequestration requires subsurface storage space for huge volumes of supercritical CO_2. The chosen storage formations must be capable of retaining the stored CO_2 for hundreds to thousands of years. A superior geological storage site must possess three essential characteristics: adequate pore space, well-

connected permeability, and a low risk trapping formation. UW and SPIERCE propose that the Ordovician Majiagou Formation (in the Ordos Basin, northern Shaanxi Province, China) has the potential to be a superior geological storage reservoir.

The Ordos Basin of China is rich in energy resources: the basin is ranked first in China for coal, coalbed methane, and natural gas production, and fourth in oil production. The coal deposits in the Ordos Basin account for 39% of total Chinese coal reserves (3.98 trillion tonnes). The mature oil fields in the Ordos Basin are excellent candidates for enhanced oil recovery via CO_2 flooding. The overlapping development of relatively new coal conversion industries with existing oil and gas industries in northern Shaanxi Province has created a unique opportunity to integrate geological CO_2 storage with CO_2-EOR. At present, many CCUS projects focus on CO_2 emitted by coal-fired power plants. The higher energy consumption/penalty and costs of CO_2 capture from coal-fired power plants have become serious technical and financial obstacles for commercial-scale CCUS and CO_2-EOR projects. In Northern Shaanxi Province, the coal conversion industry (i.e., coal to methanol, coal to olefins, etc.) provides affordable, capture-ready CO_2. Compared with other CCUS projects, the ability to use CO_2 from the coal conversion industry for CO_2-EOR and geological CO_2 storage make these projects in the Ordos Basin more cost-effective and technologically efficient.

Geological Background

With an area of 370,000 km^2, the Ordos Basin is the second largest sedimentary basin in China and covers portions of the Shaanxi, Shanxi, and Gansu provinces, and the Ningxia and Inner Mongolia autonomous regions. Tectonically, the basin lies in the western part of the North China Block and is bordered by Luliang Mountain to the east, Qinling Mountain to the south, Liupan Mountain and Helan Mountain to the west, and Lang Mountain and Yin Mountain to the north. Separated by the Great Wall, the basin is covered by the Maowusu and Kubuqi deserts in the north and the Loess Plateau in the south (Figure 1).

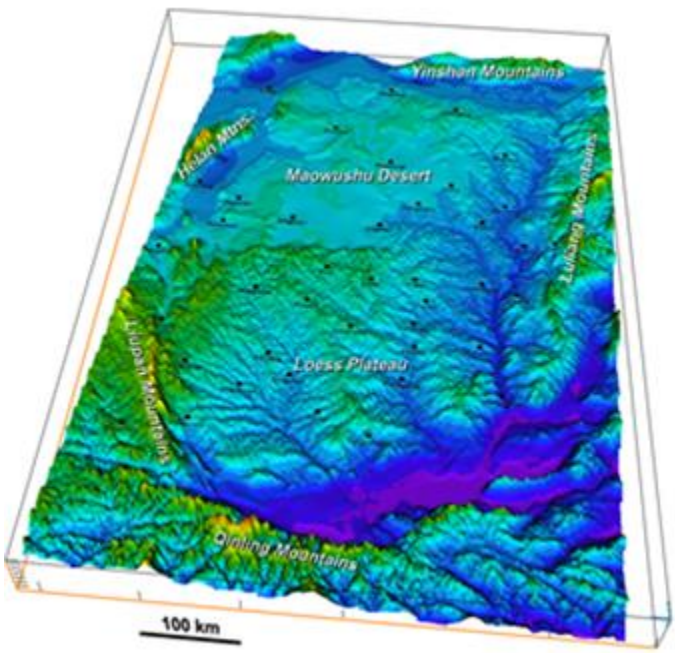

Figure 17: Geographic map of the Ordos Basin, China.

The Ordos Basin is surrounded by the Yellow River to the west, north, and east: all water systems in the basin are part of the Yellow River drainage. Most of those in the desert and plain areas are intermittent streams that typically flow into desert lakes or salt marshes. Though its surface streams have small permanent flow and poor water quality, often drying out in summer, the Ordos Basin has extensive groundwater resources.

The Ordos Basin is a cratonic basin that developed into a large stable basin during the Paleozoic, with tectonic movements dominated by regional uplift and subsidence. With the exception of uplifts and depressions that developed at the margins, the basin is characterized by a huge monoclinal structure (110,000 km^2) with a 1 to 2-degree dip to the west, called the Shaanbei Slope (Figure 2). The Shaanbei Slope is dominated by a relatively stable tectonic environment with minor regional faults and is, therefore, a most favorable structural unit for geological CO_2 storage in China.

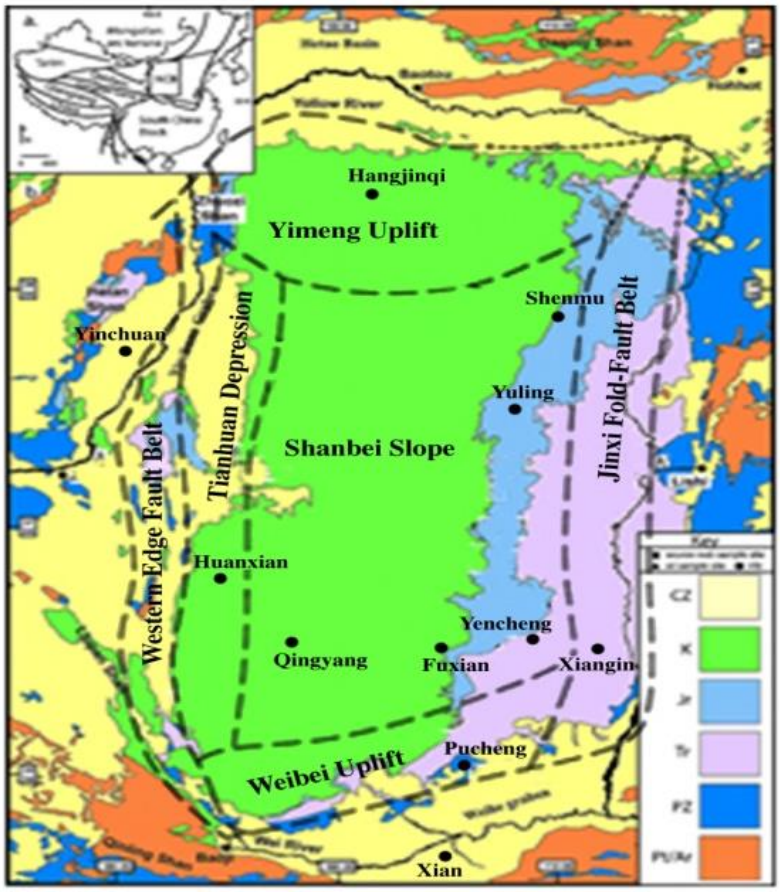

Figure 18: Geological index map of the Ordos Basin (modified from Zhang, 2004).

The basement is metamorphic Archaen and Lower Proterozoic rocks. The basin has experienced five stages of geologic evolution: 1) Mid- to Late-Proterozoic aulacogen, 2) Early Paleozoic shallow foreshore platform, 3) Late Paleozoic coastal plain, 4) Mesozoic inland basin, and 5) Cenozoic faulting along the basin margins. The Ordos Basin can be subdivided into six structural units as follows: The Yimeng Uplift, the Weibei Uplift, the Jinxi Fault-Fold Belt, the Shanbei Slope, the Tianhuan Depression, and the Western Edge Fault Belt (Figure 2).

The sedimentary strata of the Proterozoic, Paleozoic, Mesozoic, and Cenozoic are well developed in the Ordos Basin. The thickness of Paleozoic and Mesozoic sedimentary strata ranges from 2,559 m to 7,847 m (Figure 3). During the Cambrian to Early Ordovician, the Ordos Basin region was a shallow marine carbonate platform, and 300 meters to 600 meters of carbonate rocks were deposited in the main part of the Ordos Basin. During the later Early Ordovician to Middle Ordovician, the North China Block (including the Ordos Basin) experienced a large-scale marine transgression that deposited the 100 to 900 meters of the Majiagou Formation, which consists of dolomite, limestone, and evaporate rocks in the interior of the basin. Upper Ordovician, Silurian, Devonian, and Carboniferous strata do not occur within the basin, and their absence is marked by a major regional unconformity that lies between the Middle Ordovician and Pennsylvanian strata. During the 150-ma-long hiatus from the Middle Ordovician to the Mississippian, intense karstification of the Ordovician dolomites resulted in a wide distribution of collapse strata along the regional unconformity, in which the reservoir rocks of the Jingbian gas field were deposited. The average thickness of the Upper Paleozoic sedimentary rocks ranges from 800m to 1,000m and include the gas-bearing intervals of the Carboniferous Benxi Formation, and the Permian Taiyuan, Shanxi, Shihezi, and Shiqianfeng formations. During the Triassic and Jurassic, a thick terrestrial stratigraphic section consisting of lacustrine, fluvial, wetland, and deltaic strata – including shales, mudstones, coal, and sandstones with a thickness of 2,300m to 5,700 m – accumulated. The Triassic Yanchang Formation is a major oil-rich stratigraphic section in the Ordos Basin. During the Early Cretaceous, 100m to 1,200m of eolian sediments were deposited in the Ordos Basin. In the Cenozoic, climate change brought drought to the Ordos, and the basin uplifted again, accumulating more than 200 meters of loose sediment.

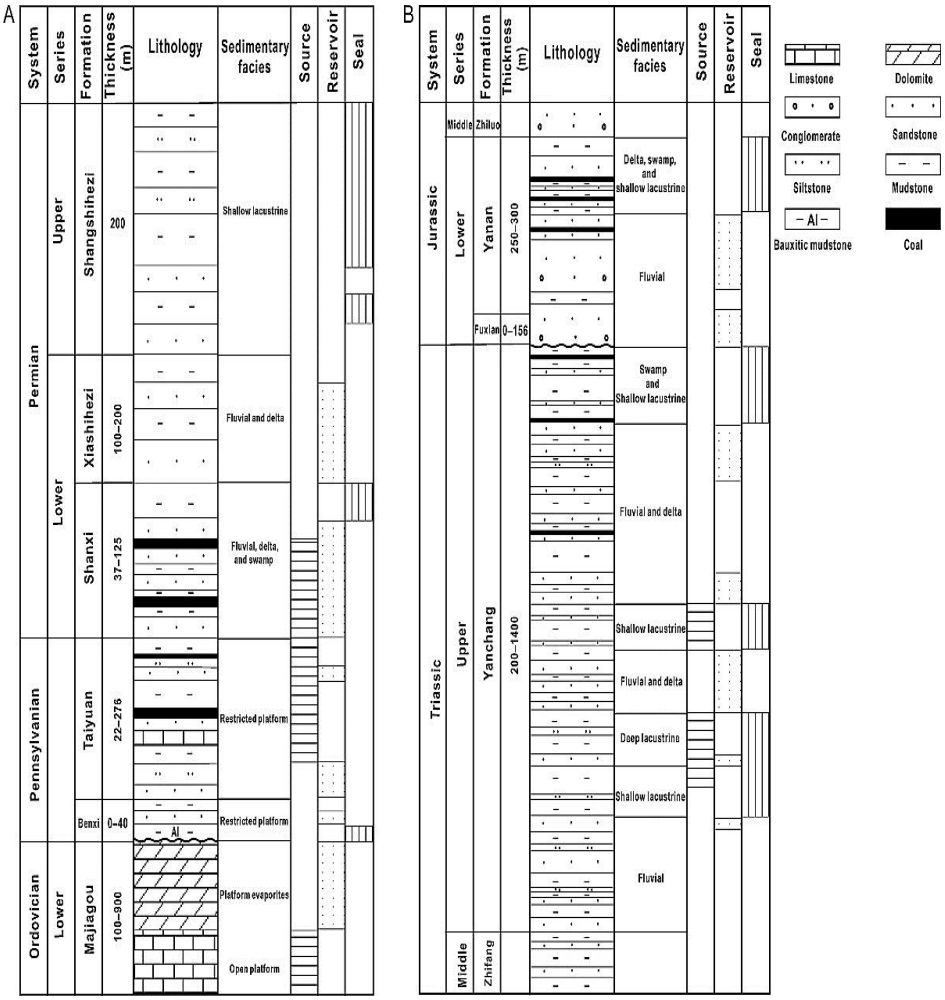

Figure 19: Stratigraphic columns show the formation thickness, depositional environments, and reservoir and trap rocks in the Ordos Basin, modified from Yang et al., 2005.

The potential geological CO_2 storage reservoirs in the Majiagou Formation lie beneath a 2,000+ meter-thick sequence of Mesozoic rocks containing a multitude of low-permeability sealing lithologies. The Majiagou carbonate reservoir at the study site is more than 700 meters thick and is located at depths where pressures and temperatures are well above the supercritical point of CO2 (31 °C and 7.4MPa). The targeted reservoir contains high-salinity brines (20,000–50,000 ppm) with little or no economic value at present. The Majiagou reservoir is laterally continuous, as inferred from well logs, and cores show that porosity ranges from 1% to 15% with an average measured porosity of 8%: permeability ranges from 1–35 md.

Oil, Gas, and Coal Resources in the Ordos Basin

As a key national energy and chemical industry development base, the Ordos Basin is the largest energy supplier in China, accounting for nearly 6%, 13%, and 39% of national natural gas, coalbed methane, and coal reserves, respectively. The basin's crude oil reserves rank fourth in China. Oil, natural gas, coal, coalbed methane, and sandstone-type uranium are found in different tectonic structures and various sequences of Paleozoic to Mesozoic strata. While the oil reservoirs lie mainly in the Triassic and Jurassic sections in the southern part of the basin, gas reservoirs occur predominantly in the northern part of the basin in the Ordovician Majiagou Formation and Permian Shanxi and Shihezi formations (Figure 4). Coal resources are widely distributed in the Carboniferous, Permian, Jurassic, and Triassic stratigraphic sections. The sandstone-type uranium deposits and coalbed methane fields are located mainly at the basin margins.

More than 40 oil fields have been discovered in the basin, including Xifeng field, the largest oil field found in the past ten years, with a reserve of 400 million tonnes of crude oil. Four of China's five gas fields with reserves of at least 100 billion cubic meters are located in the Ordos Basin, including Sulige, Jianbian, Wushenqi, and Yulin gas fields (Figure 4). The Ordos Basin contains more than 8 billion tonnes of equivalent petroleum resources or about 11 trillion cubic meters of natural gas. In 2011, oil production from the Changqing oil fields was 20 million tonnes, while production from the Yanchang

Group was 12.32 million tonnes: production from these two companies together is close to the total oil production of the Ordos Basin. The annual oil production of the Ordos Basin is expected to exceed 37 million tonnes by 2020, and the annual production of natural gas is expected to reach 40 billion to 50 billion cubic meters in ten years.

The Ordos Basin contains more than 39 percent of China's coal reserves, with reserves of 3.98 trillion tonnes: of these reserves, 2.41 trillion tonnes lie less than 1,500 m deep. The coal production of the Ordos Basin was about 1.1 billion tons in 2011: six of thirteen major national coal mines are located in the Ordos Basin. The reserve of coal-bed methane in the Ordos Basin is estimated from 7.8 to 11.3 trillion cubic meters.

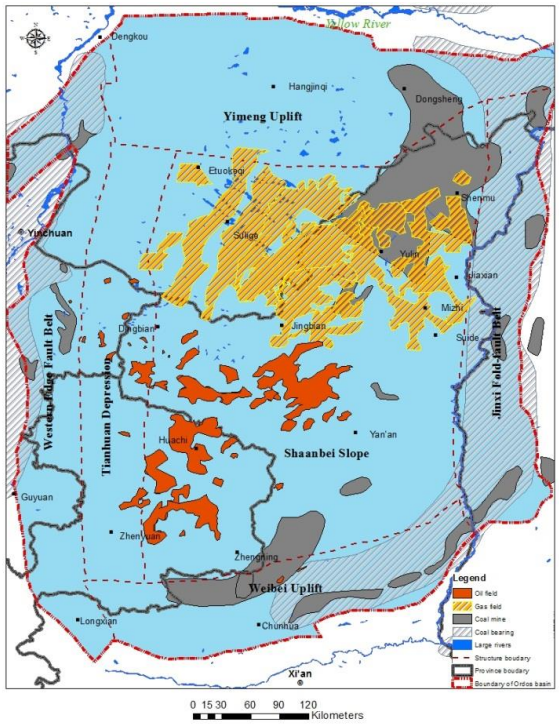

Figure 20: Map showing oil, gas, and coal fields in the Ordos Basin.

Sources of Anthropogenic CO_2 in the Ordos Basin

Along with being China's number-one energy producer, the Ordos Basin also hosts the nation's largest coal-to-chemical industry base. As more coal-fired power plants and coal-to-chemical plants have been built near the coal mines in the Ordos Basin, anthropogenic CO_2 emissions have increased correspondingly and dramatically.

Industrial sectors examined within the scope of this study include coal-fired power plants, coal conversion plants (methanol, acetic acid, diesel, ethylene oxide), cement plants, iron and steel plants, petroleum refining facilities, and ammonia plants. The CO_2 emissions calculation methodology is based on IPCC Guidelines for national greenhouse gas inventors and based on available plant capacities and productivity, as noted below:

$$(ECO_2)_{ji} = (EF)_{ji} * (P_1)_{ji}$$

$$(ECO_2)_{ji} = (EF)_{ji} * (P_2)_{ji} * (A)_{ji} * (T)_{ji}$$

$$(ECO2)ji = \sum_{j}^{n} \sum_{i}^{m} (ECO2)ji$$

Where, $(ECO_2)_{ji}$ is the estimated annual CO_2 emissions of the ith emission source within the jth industry sector; $(EF)_{ji}$ is the emission factor of the ith CO_2 emission source within the jth industry sector; $(P_1)_{ji}$ is the production yield of the ith CO_2 emission source within the jth industry sector; $(P_2)_{ji}$ is the production capacity of the ith CO_2 emission source within the jth industry sector; $(T)_{ji}$ is the production rate, full load time (hour); N is the number of industry sectors; and M is the number of factories within sector i.

CO_2 emissions calculated for cement plants, refineries, iron and steel facilities, and ammonia plants are based on reported productions while productive capacity was used for power plants and a mixture of those ethylene oxide and ethylene plants. Table 1 shows CO_2 emission factors applied to each of these sectors.

Table 2: Estimated emission factors of different stationary CO_2 emission sources.

Sector	CO_2 Emission Factors			
Cement (kt/kt)	0.882[a]	0.867[b]	1.111[c]	1.102[d]
Power Plant (kt/Gw.h)	1[e]	0.5[f]	0.4[g]	
Steel & Iron (kt/kt)	1.27			
Refinery (kt/kt)	0.219			
Ethylene (kt/kt)	2.541			
Ammonia (kt/kt)	3.8			
Ethylene Oxide (kt/kt)	0.458			
Hydrogen (kt/kt)	6.15			
a Dry process 1; b Dry process 2; c Wet process 1; d Wet process 2;				
e Coal power plant; f Gas power plant; g Oil comb, turbine combustion				

We developed a map of the stationary CO_2 sources in the Ordos Basin, including largest stationary sources that emit at least 0.1 Mt of CO_2 per year, including coal-to-chemical plants, coal-fired power plants, refining facilities, cement plants, and ammonia plants. As a result, this analysis does not consider all anthropogenic CO_2 emissions and specifically does not include those from small industrial CO_2 point sources such as transportation, direct energy use in the commercial and residential building sector, land use, agriculture, and similar activities.

Enterprise locations including city and province were taken from web searches, and latitude and longitude coordinates were assigned based on the center of the corresponding city.

Results of this inventory indicate that more than 43 large stationary CO_2 point sources in the Ordos Basin emit at least 0.1 Mt per year. Annually, CO_2 emissions from these sources total an estimated 45 mt. Among these emissions, there are 40 mt from the methanol plants (Table 2). These 45 mt of captured CO_2 have a high concentration (>95%) and are ready to be used for CO_2 flooding in the Ordos Basin (Figure 5).

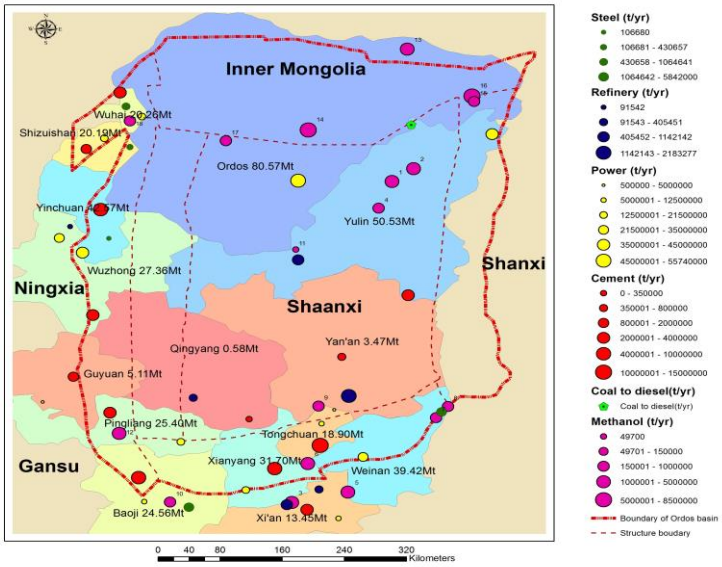

Figure 21: Map of large stationary CO_2 point sources by type and annual emissions in the Ordos Basin.

Table 3: List of the CO_2 emissions from the major methanol plants in the Ordos Basin, based on the various web pages and news releases.

Province	Plant	CO_2 Emitted, T	Load Stock
Shaanxi	Yanzhou Group Yulin Energy & Chemical CO. Ltd	3,852,900	Coal-base
Shaanxi	Shenmu Chemical Industry CO. Ltd, Shenhua Group	3,852,900	Coal-base
Shaanxi	Xianyang Chemical Engineering CO. Ltd	3,852,900	Coal-base
Shaanxi	Yulin Natural Gas Chemical Engineering CO. Ltd	313,110	Gas-base
Shaanxi	Shaanxi Weihe Coal Group	3,852,900	Coal-base
Shaanxi	Shaanxi Coke Chemical CO. Ltd	1,194,300	Coal-base
Shaanxi	Shaanxi Heimao Coke Chemical CO. Ltd	173,000	Coal-gas-base
Shaanxi	Shaanxi Longmen Coal Chemical CO. Ltd	346,000	Coal-gas-base
Shaanxi	Shaanxi Huangling Coal Chemical CO. Ltd	173,000	Coal-gas-base
Shaanxi	Shaanxi Baoji Xinrong Chemical CO. Ltd	298,000	Coal-base
Shaanxi	Changqing Oil Company Jingbian Mathnol Plant CO. Ltd	49,700	Gas-base
Gansu	Huating Zhongxun Coal Chemical Engineering CO. Ltd	3,582,900	Coal-base
Inner Mongolia	Iner Mongolia Yuanxing Energy CO. Ltd	3,582,901	Coal-base
Inner Mongolia	Iner Mongolia New Energy CO. Ltd, ENN Group	8,061,525	Coal-base
Inner Mongolia	Dongfang Energy CO. Ltd, Yidong Group	173,000	Coal-gas-base
Inner Mongolia	Jiutai Energy Inner Mongolia CO. Ltd	5,971,500	Coal-base
Inner Mongolia	Western Coal Chemical Wuhai Energy CO. Ltd, Shenhua	173,000	Coal-gas-base
Inner Mongolia	Wuhai Cke, Wuhai Energy CO. Ltd, Shenhua Group	519,000	Coal-gas-base
	Total of CO_2 emissions from coal/gas chemical	40,022,536	

Geological CO_2 storage site characterization

The geological CO_2 storage site characterization projects carried out by UW CMI team and Chinese partners have identified that two problems: (1) reservoir pressure management through the producing displaced fluid; (2) uncertainty in numerical simulation and performance assessment due to lack of realistic documentation of 3-D heterogeneity of geological and petrophysical parameter. Through the course of the projects, a practice work flow (Figure 6) has been established to solve these problems.

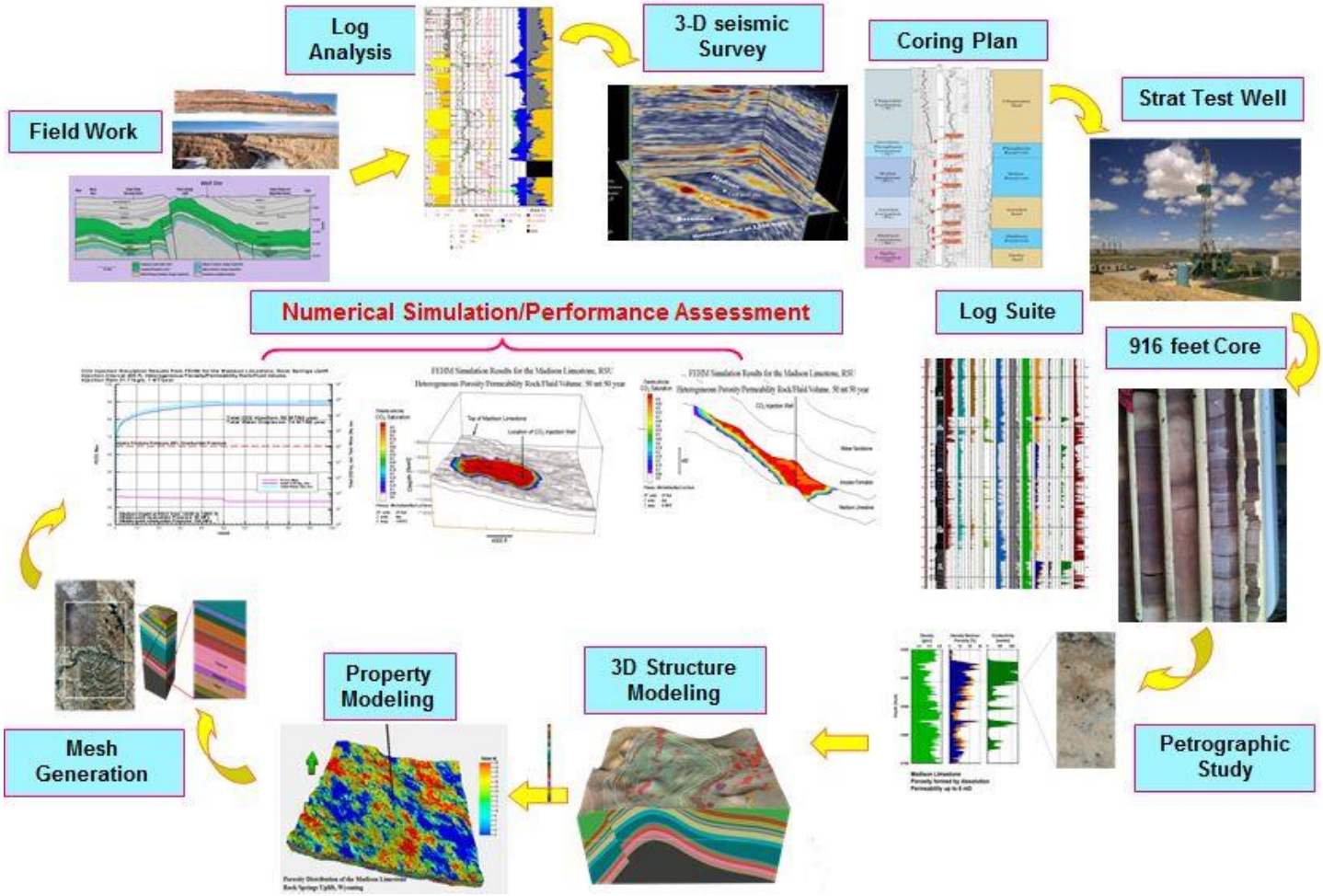

Figure 22: Work flow chart for a detailed 3-D geological CO2 storage site characterization.

First, all available surface and subsurface information pertaining to the storage reservoirs, confining layers, and structural setting was collected. Using this existing data, a priority storage site and targeted reservoir and confining layer intervals were selected for further investigations.

Second, on the basis of existing data, the preliminary storage capacity of the targeted reservoirs could be estimated by a volumetric approach and numerical simulation. The lack of the necessary data was identified, and data acquisition strategy was determined.

Third, to obtain the information essential to characterization strategy, a stratigraphic test well was drilled, and a 3-D multi-component seismic survey is acquired to describe reservoir and confining layer characteristics in three dimensions within the targeted storage domain. A complete log suit from the surface to the bottom of the hole, and drilling cores covering targeted reservoirs and confining layer were collected. The formation fluid was sampled. The well tests, such as pressure buildup and DST, were conducted. The results of outcrop observations, core analyses, log and seismic interpretations, and fluid chemistry were used to determine and delineate the structure features, stratigraphic and lithological facies distributions, formation fluid characteristics, and fracture swarm developments.

Fourth, integrated 3-D seismic attributes with log interpretations, core observations, laboratory measurements, and in-situ well tests were used to construct geological structural, litho-facies, porosity, permeability, and fractural 3-D models to characterize the heterogeneities of each property in the three dimensions. Within these structural and property models, it is now possible to isolate individual reservoir horizons and construct maps of the distribution of seismic attributes and associated petrophysical properties, most importantly porosity and permeability. Through integrating the results from seismic attribute distributions, log interpretations, and core analysis, the three-dimensional configuration of the petrophysical properties of the storage reservoir and confining layer intervals could be determined and delineated. Such 3-D configuration significantly increases the resolutions of petrophysical property distribution in both vertical and horizontal directions, and substantially reduces the geological uncertainties of storage and sealing capacity assessments (i.e., numerical simulation of CO_2 injection scenarios).

Fifth, a computation mesh was generated from the structural and property models. Variable gridding sizes (fine near the injection site and coarse far away from the injection site) were adopted to capture the injected fluid migration pathway and reservoir pressure response, and to reduce the computational and convergence challenges. A series of injection scenarios were simulated to evaluate the injectivity, injected fluid migration and distribution, pressure response, storage capacity, and confining layer integrity.

Sixth, with all above information, detailed probabilistic assessment and a monitoring verification and accounting plan can be developed for the storage project. The commercial project design should include a displaced fluid management plan if the risk assessment suggests a problem with displaced fluids. Commercial volumes of injected CO_2 may displace large volumes of saline water, which may migrate over large areas, diverge from predicted flow pathways, interfere with adjacent mineral estates, and/or damage potable water sources if left unmanaged. The injected CO_2 and ambient fluids are constrained at optimum pressures by producing and treating displaced brine at surface facilities, thereby containing the fluids within a defined monitored volume.

The work flow chart above provides a strategy to evaluate a potential commercial-scale geological CO_2 storage site. Following this work flow will result in a detailed geological CO_2 storage site characterization and a certified storage site for developing a commercial-scale storage project. This investigation processing was used for geological CO_2 storage capacity assessments in both Wyoming Laramide basins and the Ordos Basin.

Geological structural modeling of the Ordos Basin

A regional 3-D geological model was constructed for the Ordos Basin utilizing well logs, isopach maps, and geological data assembled from published articles. The model covers a 420 by 750 km area of the Shaanbei Slope Block and was built using the commercial software EarthVison®. No faults were included in this geological structural model. The gridding sizes for the x, y, and z axes are 69 x 99 x 71, or 5000 x 5000 x 100 m, respectively, and the 2-D and 3-D minimum tension griddings were used to construct this model. Figure 7a shows the incline view to the southeast of the geological structural model for the Ordos Basin. Zone 2 represents the Majiagou Formation, and Zone 9 represents the Triassic sequence. Figure 7b shows the Majiagou Formation dipping 1 to 2 degrees to the west, with gentle structures favorable for geological CO_2 storage. This 3-D geological structural model was used to calculate the CO_2 storage capacity of the Majagou Formation using a volumetric approach.

A smaller 3-D geological model 50 x 50 km centered near Hengshan city was extracted from the regional geological structural model. This smaller scale model was used to generate a 3-D computational mesh for the Majiagou CO_2 injection simulations.

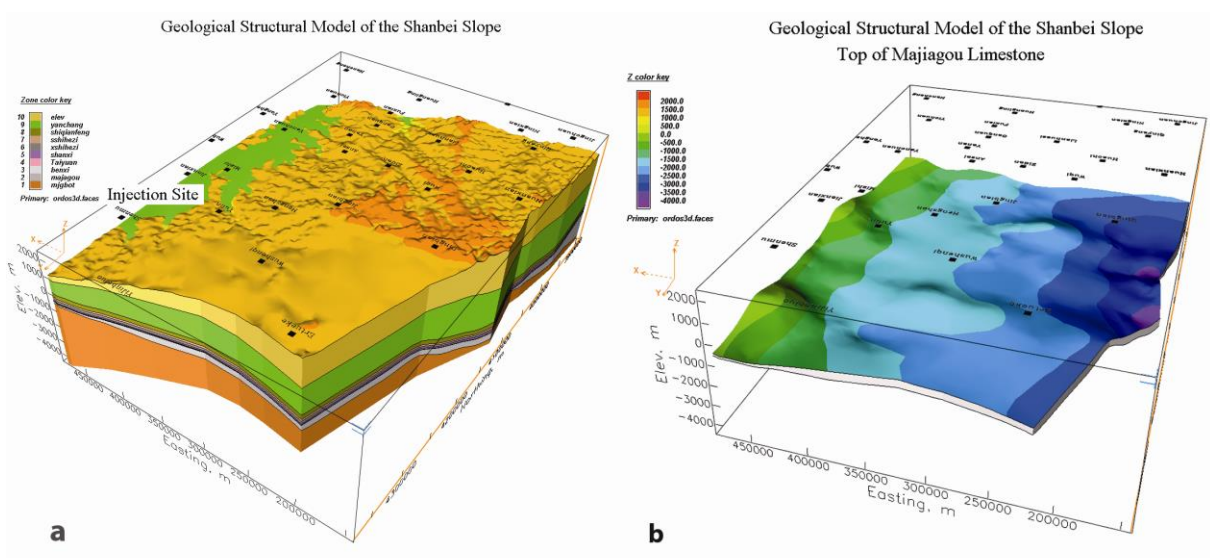

Figure 23: Incline view to southeast of the geological structural model for the Ordos Basin with the location of the potential injection site near the Yulin City (a); the 3-D view of Majiagou Formation dipping 1 to 2 degrees to the west, with gentle structures favorable for geological CO_2 storage (b). From Jiao et al., 2010.

Storage capacity based on the volumetric approach

USGS Open-File Report 2009-1035 [2] provides a formula for assessing the CO_2 storage capacity called the Total Known Volume (TKV). TKV is based on the total volume of pore space within the targeted reservoir. The formula for the TKV calculation is as follows:

$$S_{TKV} = T_a * T_i * N_{tp} * \Theta * C_e * C_f * \rho_{CO2},$$

where S_{TKV} is the storage resource of the assessed reservoir, in million tonnes; T_a is the trap area in km^2; T_i is the interval thickness of the storage formation in m; N_{tp} is a fraction of T_i; Θ is porosity, fraction; the product (T_i * N_{tp}) is commonly called net pay; C_e is the storage efficiency factor (fraction of the pore space that can be occupied by CO_2); C_f is a conversion factor, (using the units given here, it is 1); and ρ_{CO2} is the density of CO_2 in metric tons per cubic meter (metric tons/m^3).

In order to use the above equation to calculate the CO2 storage capacity of the Majiagou Formation, the trap area (Ta) must first be defined. In other words, we must determine the upper depth limit and the lower depth limit of the targeted reservoir. The pressure and temperature required for CO2 to be a supercritical fluid are typically met at depths greater than 800 m (2,600 ft) under a normal hydrostatic pressure gradient. To reduce the chance that CO2 may migrate to a pressure regime and temperature conditions where it could convert from the supercritical state to liquid and vapor, a minimum storage depth of 1,000 m (3,280 ft) was chosen in the study. The minimum storage depth sets the upper depth limit of a potential CO2 reservoir. The lower depth limit for CO2 storage is more arbitrary than the upper depth limit. If the CO2 pressure at the wellhead is 15 MPa (2,175 psi), and CO2 density is 0.65 g/cm3, the CO2 pressure will be 41 MPa (6,000 psi) at the bottom of a 4,000-meter-deep (13,120 ft) well. Therefore, CO2 injected at this depth will displace normally pressured formation water without additional compression. In this study, 4 km (13,120 ft) was chosen for the maximum storage depth. Assuming that 25% of the formation thickness is available, then, the 14,500 km3 of the total volume of rock and pore spaces available for the CO2 storage (Ta*Ti*Ntp) is determined from the EarthVision geological structural model for the Majiagou Formation.

The lognormal porosity distribution with a mean of 0.085, a standard deviation of 0.02, and a skewness of 0.44 was determined from all available measured data. For a saline aquifer, the upper limit on the storage efficiency factor was related to the irreducible water saturation of the trap in the presence of CO2. Values for irreducible water saturation in petroleum reservoirs are not well known, but they probably range from a minimum of about 0.2 in gas reservoirs to about 0.6 in oil reservoirs. The results of the CO2 injection simulation using Finite Element Heat and Mass Transfer (FEHM) show that the majority of CO2 saturation ranges from 0.1 to 0.6. The storage efficiency in this study was chosen between 0.1 and 0.6. Using the above parameters, a Monte Carlo simulation from Goldsim with 10,000 realizations was set up for the Majiagou Formation between depths of 1,000 m and 4,000 m. Figure 9 shows the probability density of the CO2 storage capacity of the Majiagou Formation in the Ordos Basin. CO2 storage capacity ranges from 60 to 700 Gt, with a mean of 287 GT (Figure 8). Therefore, the Majiagou Formation has sufficient storage capacity to accommodate decades of CO2 emissions generated by the coal industries in the Ordos Basin.

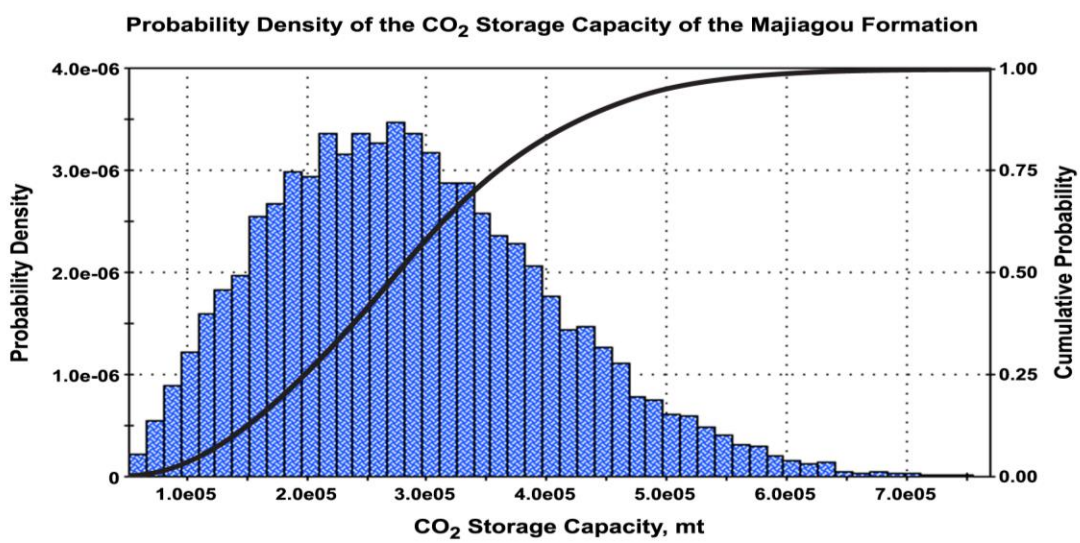

Figure 24: The probability density of the CO_2 storage capacity of the Majiagou Formation in the Ordos Basin. A cumulative probability of 25% yields a value of 200 Gt. This indicates that for this particular distribution, we have a 25% chance of storing 200 Gt of CO_2 or less. Put another way; this indicates that we have a 75% chance of storing at least 200 Gt CO_2 in the Majiagou Formation in the Ordos Basin, China.

Generation of a 3-D computational mesh

Following the logic and methodology outlined in Miller et al. 2007, a computational hydrostratigraphic mesh was created from the 50 by 50 km geological structural model described above. In this computational mesh, the simulation cells or nodes were aligned to follow the curvature of the unit interfaces and do not stair-step in the manner of a traditional finite element grid. This allows for a more accurate calculation of CO_2 moving along the caprock in the up-dip direction. The numerical mesh presented in this paper is near Henshan city and consists of a block that is 50 x 50 km in map view within the 420 x 750 km regional geological structural model of the Shaanbei Slope, with the elevation extending from 200 m above sea level to 3200 m below sea level. Grid spacing is 250 m in the x and y directions at the injection area and increases logarithmically away from the injection area. The grid spacing in the vertical direction is 50 m at the injection interval and 100 m both above and below the injection interval. The total mesh consists of 320,000 nodes with 1.92 million volume elements.

Carbon dioxide injection simulation setups

Simulations of CO_2 injection were run on the Los Alamos National Laboratory Finite Element Heat and Mass Transfer (FEHM) multiphase porous flow simulator. FEHM has been used successfully for many multiphase applications, including isotopic fractionation in the vadose zone, methane hydrate dissolution and transport, geothermal energy analysis, and simulations of CO_2 injection into saline aquifers.

Initial conditions for the model domain included a geothermal gradient of 26 °C/km with a domain bottom temperature of 120 °C and a domain top temperature of 47 °C, and a hydrostatic pressure ranging from 13 MPa at the top of the modeling domain, 200 m above sea level to 44 MPa at the bottom of the modeling domain, 3200 m below sea level. Further simplifying assumptions for the 3-D injection calculations are that thermal conductivity of the rocks is constant at 0.5 W/m-K, rock density is constant at 2,650 kg/m^3, and heat capacity is constant at 1,000 J/kg-K. Relative permeability for all rocks was assigned with a residual saturation of 10% for both brine and CO_2 using a linear relationship. Capillary pressure effects were ignored; brine TDS is constant at 20,000 ppm for all formations, and water viscosity is calculated independently of brine content or dissolved CO_2. The initial dissolved CO_2 concentration was set to zero. During CO_2 injection simulation, the simulator accounts for CO_2 dissolution in water. For all simulations, the down-dip sides (west and south sides of the domain) are closed, whereas the up-dip sides (north and east sides) are open to the reservoir fluid.

In order to evaluate the impacts of injection rate, porosity, and permeability on storage capacity, reservoir pressure evolution, and CO_2 plume migration trends, a series of CO_2 injection simulations were conducted using various injection rates, porosities, and permeabilities for the targeted Majiagou Formation.

Simulations and results for the Majiagou Formation

An important consideration in the CO_2 injection simulation results from FEHM for the various scenarios is the pressure buildup during injection. A limiting value of 75% of overburden pressure was selected for all simulations in order to ensure that the Majiagou Formation and overlying sealing formations are not fractured during injection.

Various FEHM injection simulation scenarios were utilized for the Majiagou Formation, including injection rates of 0.5 Mt/year, 1.0 Mt/year, and 2.0 Mt/year, and porosities of 5% and 10%, and permeabilities of 1 and 5 md, and all within a formation thickness of 500 m (actual thickness of the Majiagou Formation at the site is more than 700 m). Using nine injection wells, the above injection rates resulted in storage capacities of 4.5, 9, and 18 Mt per year, respectively. All simulations were run for 100 years with CO_2 injection ending after the first 50 years.

Three Majiagou simulations (nine injection wells) were run with injection rates of 0.5, 1, and 2 Mt/year, at a constant porosity of 10 percent, and a permeability of 5 md (Figures 9a). As injection rates for the nine injection wells increase from 4.5 to 18 Mt per year, the reservoir pressure gradually increases from initial reservoir pressure 40 to 55 MPa but remain below 75% of the fracture pressure (60 MPa) of the Majiagou Formation in the study area. With increasing CO_2 injection, the amount of fluid displaced during CO_2 injection also increases.

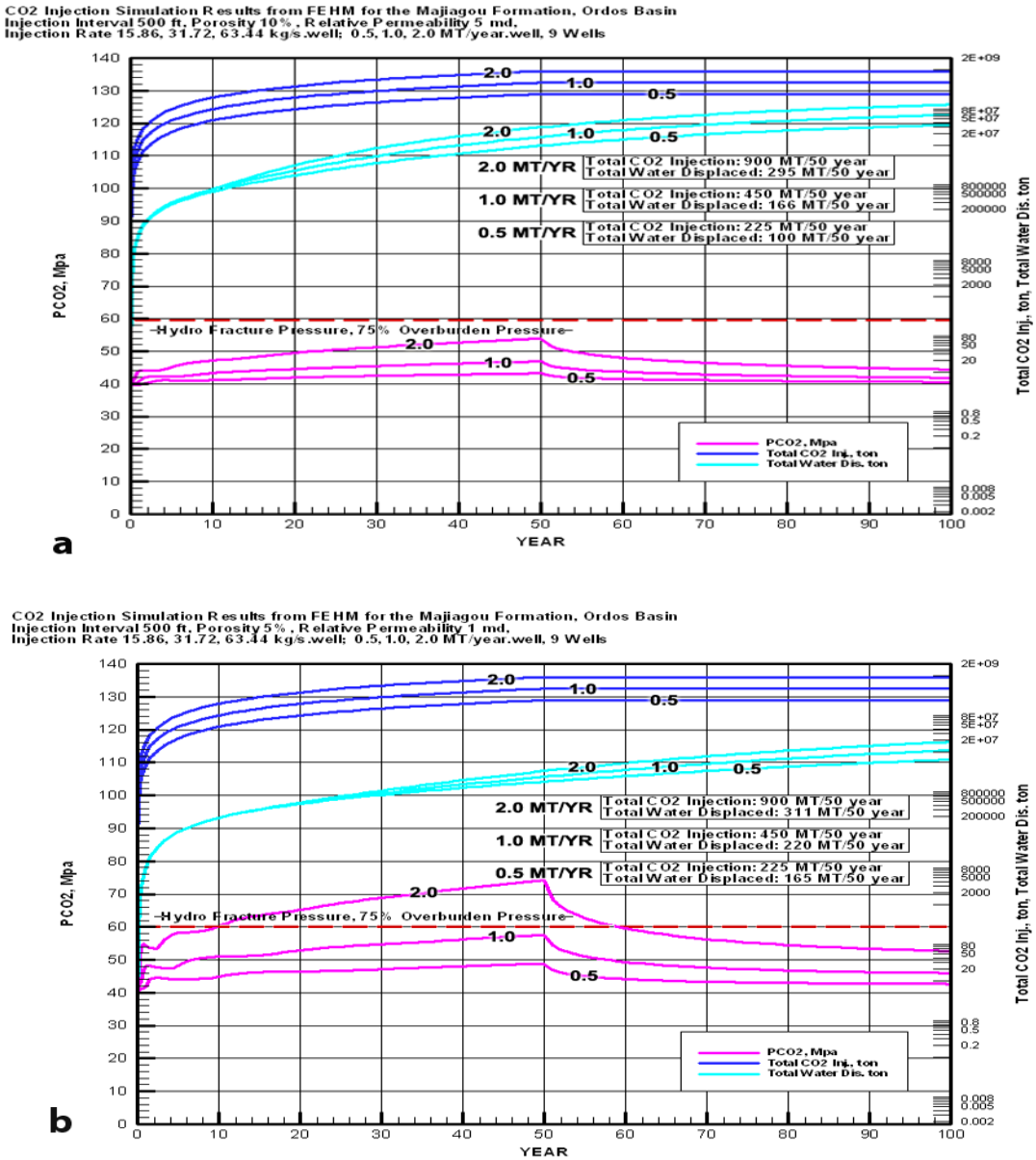

Figure 25: FEHM simulation results for the various porosities, permeabilities, and CO_2 injection rates. From Jiao et al., 2010.

Figure 9b show the results of three simulations with injection rates varying from 0.5, 1, and 2 Mt/year, at a constant porosity of 5 percent, and a permeability of 1 md. As shown by the simulation results with 10% porosity and 5 md permeability, both the reservoir pressure and volume of displaced fluid increases gradually with increasing injection rates, but the magnitude of increase is much larger. With 1 md permeability and at an injection rate of 18 Mt/year, the reservoir pressure reaches 75% of the fracture pressure of the Majiagou Formation after ten years of injection and keeps increasing to near the lithostatic pressure. In all cases, the reservoir pressure drops sharply when CO_2 injection stops (Figure 9).

Based on all available measured data, an average porosity of 10% and a relative permeability of 5 md for the Majiagou Formation were considered the most likely values for preliminary simulations. The input parameters for the most reasonable simulation were a 1 Mt/yr per well injection rate, 10 % porosity, and 5 md permeability. Using this set of parameters, results from the 50-year injection simulation show that a total of 450 Mt of CO_2 can be injected into the targeted reservoir while a total of 166 Mt of pore fluids will be displaced. Furthermore, the targeted reservoir pressures remain well below the 75% of fracture pressure limit (Figure 9b). Simulation results suggest that saturation of the CO_2 plumes ranges from 0.1 to 0.9. The modelling results from this simulation showed that the CO_2 plume produced from 1 Mt/year injection rate was relatively small after a total of 450 million tonnes of CO_2 were injected (Figures 10a and 10b). The CO_2 plume remained within the 16 by 15 km injection area after 50 years of CO_2 injecting and stayed within an area of 17.7 by 16 km after 100 years or 50 years post injection (Figures 10c and 10d).

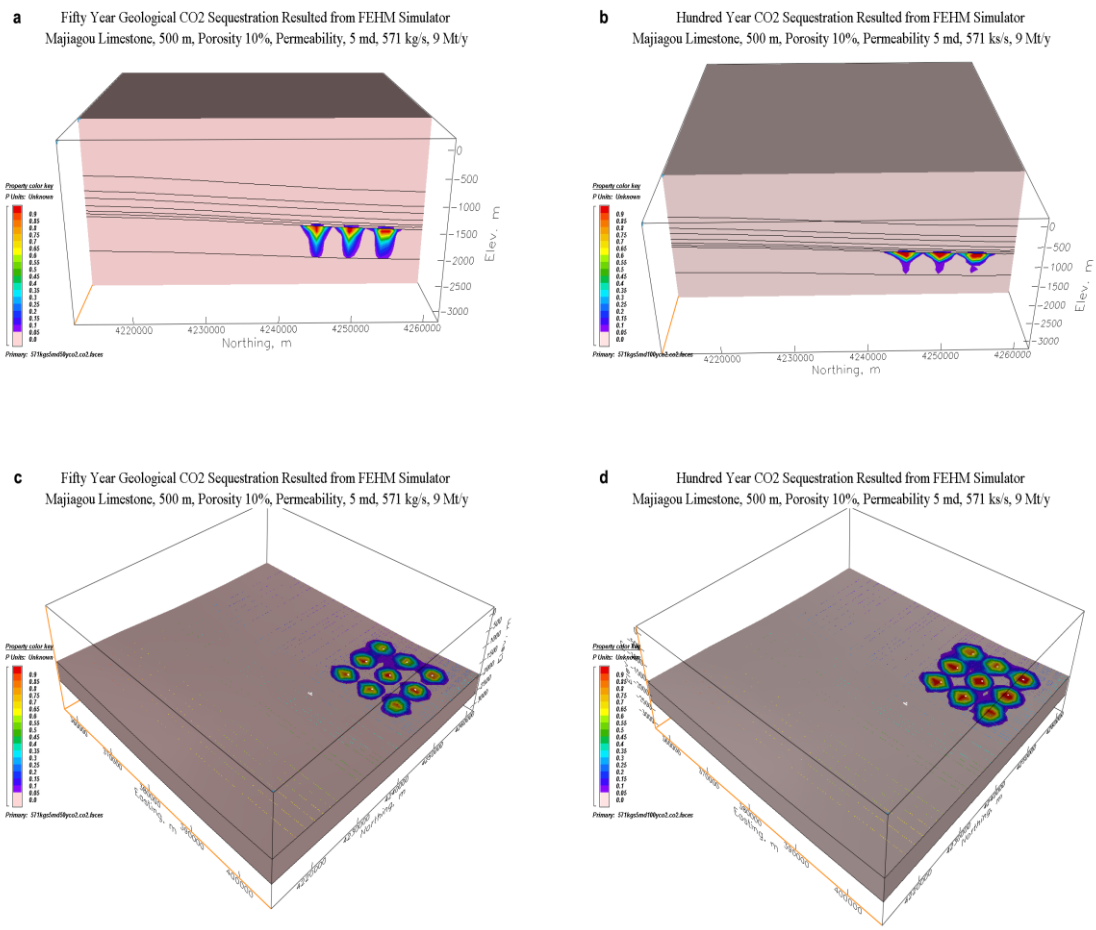

Figure 26: Three-dimensional view of the CO_2 plume distributions after 50 years of injection and 50-years post-injection.

Developing a Reservoir Management Strategy for the Bohai Bay CCUS Project

The results from the reservoir management strategy (RSU) geological CO_2 storage site characterization study demonstrate that injecting large volumes of CO_2 into saline reservoirs will result in significantly increased formation pressure, with pressure changes depending on the amount of fluid injected, injection rate, reservoir characteristics (effective porosity, relative permeability, geomechanical properties) and natural fractures. Without proper reservoir management, the increased pressure could potentially result in significant reductions of storage capacity and injectivities, geomechanical impacts such as confining layer breaching or fracturing leading to CO_2 and brine migration beyond the primary injection zone, and fault activation. An active reservoir pressure management strategy is essential to ensure safe and efficient operation of commercial-scale geologic CO_2 storage in saline reservoirs. A feasibility study to develop an active reservoir management strategy for the China Bohai Bay CCUS project was conducted during the fourth year of the CERC-ACTC Phase I program.

Geologic and Hydrogeologic Setting

The Bohai Bay Basin, China is a northeast-southwest trending transtensional basin. It is composed of numerous, smaller highlands and sub-basins which developed between several generations of major and minor extensional, oblique, and strike-slip faults. The Bohai Bay Basin is a textbook example of a negative flower structure; a multitude of juxtaposed half grabens and grabens bound by massive, regional strike-slip and extensional faults.

For this study, the Dongying Formation was considered as the potential injection formation. The upper portion of the Dongying Formation is comprised of fluvial-deltaic deposits. The middle lithofacies illustrate a transition to deeper water, with associated deep lacustrine, delta fan, and sub-lacustrine fan deposits. The lower portion is comprised of shoreline lake deposits (Dong et al., 2011, Zhang et al., 2008). The transgressive sequence during lower Dongying Formation resulted in a higher deposition rate and consequently is over-pressured (Li Chunguang, 2006). The reservoir pressure of the middle and upper Dongying is slightly over or normally pressured (Zhang et al., 2013). The Dongying Formation at the Dagang Oil Field (where the GreenGen Plant is located) is comprised of interbedded grayish green mudstone, green shale, and fine grain to coarse grain sandstone. The thickness of the Dongying Formation ranges from 100 to 600 m across the Huanghua Depression. At the proposed injection location, the thickness of the Dongying Formation is roughly 400 m. There are 120 m of sandstone with porosity ranging from 23% and 31%, and permeability from 200 to 900 md.

Water quality data from the Dongying formation are sparse. However, detailed water quality results are provided by Minnissale et al. (2008), for the adjacent Tertiary aquifer system. Samples collected from the lower Tertiary aquifer system may be representative of a first order approximation of the water quality of the Dongying Formation. These results indicate that salinity in the Dongying Formation in the study area range from 750 to 2,500 mg/L. Water type is sodium-bicarbonate-chloride with an alkaline to neutral pH (6.8 to 8.1). Dissolved minor and trace elements are generally less than 5µg/l. No information is given for dissolved organics, volatile organics, or radio nuclides. Dissolved gas compositions are measured to be greater than 90% methane with minor concentrations of CO_2 and N_2.

Preliminary Geologic Model

A 3-D structural model for the Tianjin GreenGen vicinity area was generated on the basis of available data (Figure 11). The GreenGen project is located at the southeast corner of the model. The fault block at the southwest of the model could be used for the CO_2 injection and reservoir fluid extraction. A CO_2 injection well is located 8 km northwest of the GreenGen Plant. A reservoir fluid extraction well is located 4 km away from the injection well in the up-dip direction. This model could be used in the next phase of the study for investigation of pressure evolution, storage capacity, injectivity, and necessary amount of fluid extraction during the CO_2 injection.

Based on existing structural examinations of the study area, a crucial consideration for potential CO_2 injection and storage site is the proximity and nature of Neogene-Quaternary faults. There are two major faults that bound the study area, the Cangdong fault to the west and Haihe fault to the north. The Cangdong fault trends NNE and dips SSW and cuts into the Neogene Minghuazhen Formation (Yang et al., 2013). The Cangdong fault is rooted into the Oligocene Dongying Formation (Yang et al., 2013). Strata to the west of the fault are Precambrian and Paleozoic while to the east of it the strata are mainly Mesozoic and Cenozoic. The Haihe fault strikes NWW and dips SSE, cutting into the Minghuazhen Formation 80-120 m (Yang et al., 2013).

The Dongying formation is divided into ten sandstone layers, interlayered with nine mudstone/shale layers. Note that a 188 m layer of mud/shale (Figure 4.1, Layers 6 and 7) could serve as potential confining layers for CO_2 containment. At this injection location, a CO_2 plume with 1.5 km radius (the estimated CO_2 plume size for 50 million tons), would not likely reach the major faults in any direction.

The tertiary aquifers in areas adjacent to the faults express a relatively higher TDS concentration, and the Paleozoic aquifers show a relatively lower TDS concentration. This has been interpreted to indicate unconfined aquifers in the faulted areas (Yang et al., 2013). Further evidence by isotope age relationships indicates that water near the fault is younger (Yang et al., 3013). In contrast, many of the regional faults in the area also serve as fault traps in younger strata. The transmissivities of the faults in the study area present a critical unknown that should be addressed in subsequent work.

The estimated salinities of the formation fluids are low, indicating that only minimal treatment would be required for agricultural and industrial use. The low concentrations of dissolved minor and trace elements also indicate that mineral extraction is not likely a possibility from these fluids. However, there is some indication that Dongying reservoir fluids may be a candidate for low-temperature geothermal development.

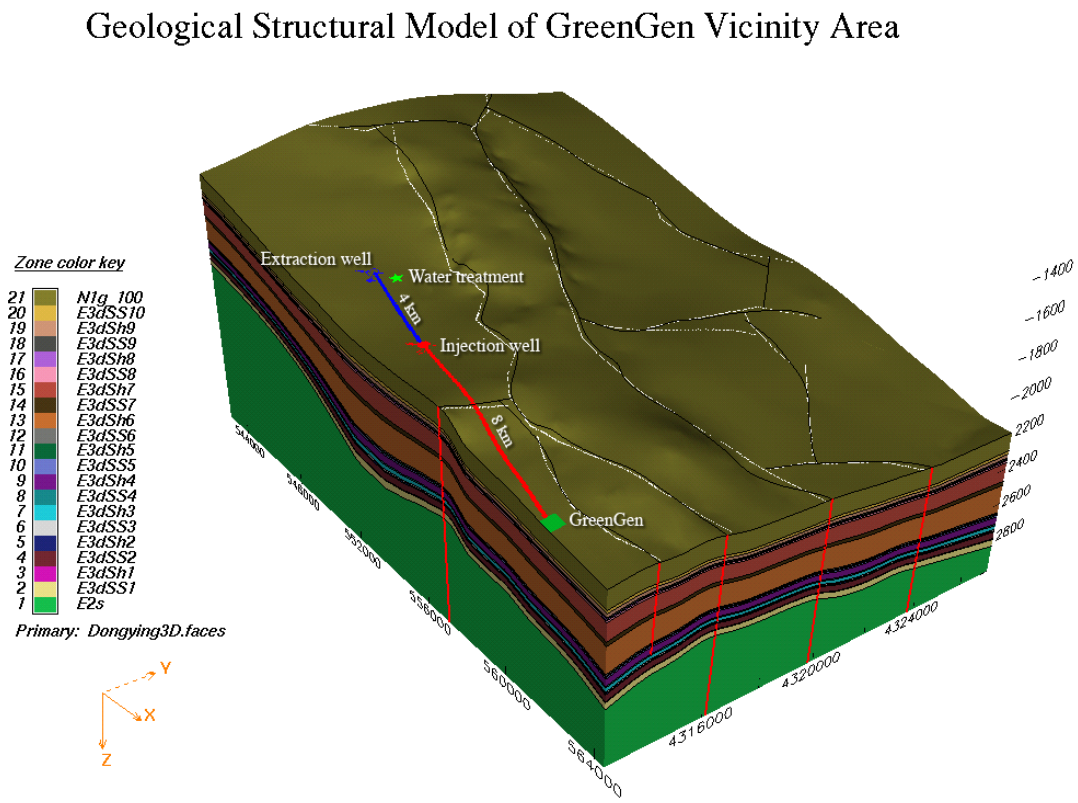

Figure 27: A 3D structural model for the Tianjin GreenGen vicinity area was generated on the basis of available data. The GreenGen project is located at the southeast corner of the model. The fault block at the southwest of the model could be used for the CO_2 injection and reservoir fluid extraction. A CO_2 injection well is located 8 km northwest of the GreenGen Plant.

Recommendations

On the basis of this preliminary assessment, the Dongying Formation looks to be an appealing candidate for further study as a potential CO_2 storage formation for the Huaneng's Tainjin GreenGen facility. This initial assessment has identified areas of critical unknowns to be addressed within a feasibility study of the area.

Recommendations for a detailed feasibility study include:

1) Acquire robust databases for the target storage domains and adjacent areas. Recommended data sources included seismic data with customized processing, and petrophysical well data including diverse log suites, cores, a VSP survey, in-bore testing (DST, injection, and rock property testing), and available geochemical data.

2) Obtain detailed water quality data from the Dongying Formation in the area of review. It is important to note that specific water quality data from the Dongying Formation, and preferably from the injection intervals are needed to determine a specific reservoir management plan. These data at a minimum should include pH, temperature, major and minor elements, and organic concentrations.

3) Use these data to generate a detailed 3-D property model used for numerical simulations and performance assessments.

4) Using the numerical simulations and performance assessments, evaluate a range of CO2 injection/storage scenarios for target reservoir intervals to determine if pressure management is required to maintain the integrity of the storage domain, or to ensure domain boundaries, evaluate the plume boundaries, volume, and rate of formation fluid removal necessary for low-risk storage.

5) Detailed examination and identification of fault types within the study area would help to subjugate risk and reduce uncertainty. To determine the structural response to injected fluids, it is of critical importance to test the fracture and slip potential of Neogene-Quaternary faults. As many of these faults bound mature oilfields, it is likely that data has already been obtained, and would be necessary for determining conservative pressure estimates and reduce the risk of failure during injection.

6) Design water production configuration. Define water production volumes and rates based on reservoir parameters developed in the 3-D property model. Plans should include transportation to a treatment facility, and options for water treatment technology.

MAJOR FINDINGS AND OUTCOMES

- Reducing uncertainty in evaluations of geological CO_2 storage site scenarios requires a robust database that allows an accurate reconstruction of the targeted storage rock/fluid volume, especially with respect to spatial heterogeneity. The results relied on a generalized regional database to populate a homogenous rock/fluid volume based on average reservoir properties yielded general insights into injection/storage characteristics but lacked specificity, resulting in performance assessments plagued by substantial uncertainty. To move from idealistic, highly generalized assessments to realistic, low-risk assessments of the China Ordos Basin and Wyoming Laramide Basins, it was necessary to acquire high-resolution data specific to the storage site of interest.
- The integration of the 3-D seismic and well log data – along with visual/ laboratory observations from the core – has substantially reduced the uncertainty attached to performance assessments and risk analysis for a geological CO_2 storage site characterization projects. As the new data from laboratory analyses, experimental determinations, and field tests become available and are integrated into the preliminary property models, uncertainty– particularly with respect to reservoir property heterogeneity was further reduced. This study establishes an exemplary strategy for dealing with CO_2 storage projects in relatively deep saline.
- The reservoir heterogeneity has a significant effect on the geological CO_2 injectivity and storage capacity of the targeted saline aquifers. Applying the diagnostic protocol for the CO_2 sequestration suggested by the Department of Energy for the FutureGen project, the geological CO_2 storage capacity of the Madison Limestone reservoir in the RSU was estimated to be 8 Gt. Using the USGS volumetric approach, the probability density of the CO_2 storage capacity of the Madison Limestone ranges from 1.6 to 14 Gt, with a mean of 6.5 GT. However, using the FEHM multi-flow numerical simulator, the CO_2 storage capacity of the Madison Limestone was estimated to be 7 Gt based on the homogeneous reservoir property (i.e., porosity 10%, and permeability 1 md). Based on the heterogeneous reservoir property, the CO_2 storage capacity of the Madison Limestone in the RSU area was estimated to be 8 Gt for the higher reservoir quality case, 7 Gt for the medium reservoir quality case, and 5 Gt for the lower reservoir quality case. Using the result from the CO_2 injection simulation for the medium reservoir quality case, the Madison Limestone and the Weber Sandstone in the RSU could store the CO_2 emission from the state of Wyoming (60 Mt/year reported) for 260 years.
- The same approach was used to assess the CO_2 storage capacity of the Ordos Basin. A Monte Carlo simulation from Goldsim with 10,000 realizations was set up for the Majiagou Formation between depths of 1,000 and 4,000 m in the Shaanbei Slope of the Ordos Basin, China. The probability density of the CO_2 storage capacity of the Majiagou Formation in the Ordos Basin ranges from 60 to 700 Gt, with a mean of 287 GT. Even with a conservative number of 60 Gt of storage capacity, the Majiagou Formation has sufficient storage capacity to accommodate over 300 years of CO_2 emissions generated by the stationary CO_2 emission sources (200 Mt/year reported) in the Ordos Basin.
- Well injectivity is highly dependent on the local permeability distribution of the targeted storage formation. Choosing the areas and intervals with higher quality reservoirs (sweet spots) are critical for a successful large-scale (over 1 Mt per year) geological CO_2 storage project. The higher quality reservoir could substantially reduce the project cost and significantly increase the CO_2 injectivity and storage capacity.
- Formation brine production around the perimeter of the storage site is necessary to keep formation pressure below the hydro fractural pressure, and reduce associated leakage, decrease seismic risks, and create the accommodation space to enhance storage capacity for CO_2 storage. The average ratio of the amount of injected CO_2 to the produced brine is 1.14. This ratio indicates that for a commercial-scale injection with limited impacts on neighboring pore space, nearly as much brine must be produced as CO_2 is injected.
- CO_2 leakage from the storage formations into the overlying rocks is highly related to connectivity of high-permeability layers and integrity of the confining layers. The preliminary results from this study suggest that the

sealing capacity of a CO_2-water-rock system may be significantly lower than previously predicted, based on the numbers used in a hydrocarbon-water-rock system. Therefore, a confining layer that trapped oil or gas for millions of years does not mean it can trap the same magnitude of injected CO_2.

Major Achievements

Meetings and Presentations

- Attended the third advanced coal technology conference in Xian (June 2012). Surdam and Jiao presented a talk titled "Reservoir Simulation of CO_2 Storage on the RSU Based on a Robust Database and an Accurate Model of Geological Heterogeneity". Jiao and Surdam also presented a talk titled "Integration of Enhanced Oil Recovery with CO_2 Storage in Mature Oil Fields of the Ordos Basin, China: Opportunities and Challenges".
- Attended the Eleventh Greenhouse Gas Control Technologies conference in Kyoto, Japan (November 2012). Two papers were presented at this conference. A feasibility study of the integration of enhanced oil recovery (CO_2 Flooding) with CO_2 storage in the mature oil fields of the Ordos Basin, China (Wand and Jiao); Characterizations of the CCUS attributes of a high-priority CO_2 storage site in Wyoming, U.S.A. (Surdam and Jiao).
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity was presented at the AAPG Annual Convention 2013, Pittsburgh.
- An oral presentation of the importance of CO_2 storage in designing strategies for the sustainable development of energy resources was presented at the Twelfth Annual Carbon Capture, Utilization & Sequestration Conference, 2013, Pittsburgh.
- An oral presentation focused on the 3-D permeability distribution of reservoir rocks in the subsurface in the RSU was presented at the Twelfth Annual Carbon Capture, Utilization & Sequestration Conference, 2013, Pittsburgh.
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity – the greatest uncertainty in numerically simulating CO_2 sequestration processes is characterizing geological heterogeneity in three dimensions, was presented at the Northwest University, Xian.
- An oral presentation that focused on the importance of CO_2 storage in designing strategies for the sustainable development of energy resources was presented at ShaanGu Power Company, Xian.
- An oral presentation of global warming and climate change – 45-million-year-old rocks in Wyoming support the concept was presented at the Shiyou University, Xian.
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity was presented at the AAPG Annual Convention 2013, Pittsburgh.
- Attended the U.S. DOE – China NDRC first CCUS initiative workshop at Beijing (April 2014). During the workshop, organizations from both countries presented their cooperation on joint CCUS works to date, along with ongoing and planned activities. In the workshop, Jiao and Northam presented the outcome from the Wyoming and Ordos Basin CCUS projects.
- Attended GHGT 12 in Austin, Texas (November 2014): At the meeting, Jiao and Zhou presented the research results from a feasibility study of the geological CO_2 storage in the Ordos Basin. Luo and Zhou presented a paper titled "The Ordos Basin: A Premier Basin for Integrating Geological CO_2 Storage with Enhanced Oil Recovery Projects in China".
- Visited the Huaneng Clear Energy Research Institute, Shaanxi Provincial Institute of Energy Resources and Chemical Engineering, Yanchang Petroleum Group, Shaanxi Coal Group, and Changqing Petroleum Company (February 2015) to share the current CCUS project status, address the challenges, and discuss more collaboration opportunities. Highly productive discussions about information transfer and the design of potential cooperative projects for CERC-ACTC Phase II between Wyoming, Shaanxi, and Huaneng Clean Energy Research Institute were further finalized. A major point of these discussions was to promote an integrated CCUS demonstration project in China.
- During the second quarter, 2015, the School of Energy Resources at UW hosted three delegations of Chinese partners: the Shaanxi delegation, led by provincial Vice Governor Wang Lixia, the Shanxi delegation, led by provincial Governor Li Xiaopeng, and SPIERCE delegation, led by Director Zhou Lifa. During the visits, the current CCUS project status, challenges, and future collaboration opportunities were discussed. Discussions regarding broad cooperation opportunities in clean energy and low carbon economy developments, and the design of potential cooperative projects for CERC-ACTC Phase II between Wyoming, Shaanxi, and Huaneng Clean Energy Research Institute were further finalized. A main purpose of the discussions was to promote an integrated CCUS demonstration project in China.

- In the third quarter, 2015, the UW team attended three meetings, UW CO_2 Conference at Casper, Wyoming, DOE Carbon Storage R&D Project Review Meeting at Pittsburgh, and Fifth China (Taiyuan) International Energy Industry EXPO, Low Carbon Development Summit at Taiyuan, China. At the Low Carbon Development Summit, Mark Northam was the keynote speaker and gave a talk on "Wyoming's energy resources – challenges and opportunities", Jiao Zunsheng presented a talk on "CCUS technology is vital to a sustainable energy future – the UW WYCUSP and CERC projects review".
- In the fourth quarter, 2015, the UW team attended three meetings, CERC-ACTC annual meeting at Jackson Hole, Wyoming, fifth International Advanced Coal Technology Conference, and 2015 U.S.-China CCUS Xinjiang Workshop. At CERC-ACTC annual meeting, Dr. Jiao presented the results from the Theme 6 study, and briefed UW and its partners on the objective and work plans of the Phase II CO_2-EOR proposal to CERC-ACTC. At the fifth International Advanced Coal Technology Conference, Director Kipp Coddington gave a talk on the impacts of regulatory and policy decisions on markets and research and technology investment decisions. At the 2015 U.S.-China CCUS Xinjiang Workshop, Dr. Jiao hosted a business-to-business panel discussion focused on creating CCUS hubs and building open-access pipelines in Xinjiang and the necessity of enabling incentives and policy.

Workshops

- UW and Chinese CERC-ACTC partners organized a workshop at Xian (June 2012). The CERC teams from both countries presented their progress, challenges, and plans for the CCUS projects from Wyoming, Illinois, Ordos, and Qinshui Basins. UW and Chinese partners—SPIERCE and Yanchang Petroleum Group—presented the progress of the stationary anthropogenic CO_2 resource inventory, geological CO_2 storage site characterization, and CO_2-EOR feasibility study in both the Wyoming basins and Ordos Basins.
- Attended the CERC-ACTC workshop held at Wuhan (May 2014). At the workshop, the CMI team presented the research results from both the Wyoming RSU geological CO_2 storage site characterization project and the feasibility study of the geological CO_2 storage in the Ordos Basin. Lessons learned, and challenges from current CCUS projects were exchanged between the U.S. and Chinese partners. During the workshop, the potential joint demonstration projects were also identified for CERC-ACTC Phase II.

List of Publications

- Jiao Z., R. Bentley, Y. Ganshin, F. McLaughlin, and S. Quillinan, 2015, Sealing capacity investigations of the multiple confining layers at the Rock Springs Uplift geological CO_2 storage site, DOE Pittsburgh CO_2 Conference, 2015
- Jiao Z., L. Zhou, R. Gao, T. Luo, H. Wang, H. Wang, F. McLaughlin, R. Bentley, and S. Quillinan, 2014, Opportunity and challenge of integrated enhanced oil recovery using CO_2 flooding with geological CO_2 storage in the Ordos Basin, China: in proceeding of the 12th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 63 (2014), p. 7761-7771.
- Luo T., L. Zhou, Z. Jiao, Y. Bai and S. Wang, 2014, The Ordos Basin: a premier basin for integrating geological CO_2 storage with enhanced oil recovery project in China: in proceeding of the 12th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 63 (2014), p. 7772-7779.
- Jiao Z., R. Surdam C., 2013, Advances in estimating the geological CO_2 storage capacity of the Madison Limestone and Weber Sandstone in the Rock Springs Uplift by utilizing detailed 3-D reservoir characterization and geological uncertainty reduction: in Surdam edit, Geological CO_2 storage characterization, Springer Publication, p. 191-232.
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- Wang Y., Z. Jiao, R. Surdam, L. Zhou, R. Gao, Y. Chen, T. Luo, and H. Wang, 2013, A feasibility study of the integration of enhanced oil recovery (CO_2 flooding) with CO_2 storage in the mature oil fields of the Ordos Basin, China: in proceeding of the 11th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 37 (2013), p. 6846-6853.
- Jiao Z., R. Surdam C. L. Zhou, and Y. Wang, 2013, A feasibility study of the integration of geological CO_2 storage with enhanced oil recovery (CO_2 flooding) in the Ordos Basin, China: in Surdam edit, Geological CO_2 storage characterization, Springer Publication, p. 271-294.

- Jiao Z., R. Surdam, Y. Ganshin, R. Bentley, and M. Garvia-Gonzalez, 2012, Documented subsurface three-dimensional geological heterogeneity in the Weber/Tensleep sandstone and Madison Limestone: Wyoming's highest-priority CO_2/hydrocarbon storage and production reservoir: AAPG 2012 Annual Convention, Long Beach.
- Surdam C. R. Z. Jiao, Y. Ganshin, and R. Bentley, 2012, The Rock Springs Uplift: a premier CO_2 storage site in Wyoming: Carbon Management Technology Conference CMTC paper 151216.
- Deng H., P. Stauffer, Z. Dai, Z. Jiao, and R. Surdam, 2012, Simulation of industrial-scale CO_2 storage: multi-scale heterogeneity and its impacts on storage capacity, injectivity and leakage: International Journal of Greenhouse Gas Control 10 (2012), p. 397-418.
- Surdam R., Z. Jiao, Y. Ganshin, R. Bentley, and M. Garvia_Gonzalez, 2012, characterizations of the CCUS attributes of a high-priority CO_2 storage site in Wyoming, USA: in proceeding of the 11th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 5 (2012), p. 1-8.

Collaboration

The Shaanxi/Wyoming Partnership is the product of years of cooperation and collaboration between the UW CMI, SPIERCE, YPG, and NWU. The SPIERCE has the strong support of the provincial government, especially the Provincial Development and Reform Commission, and Shaanxi Science and Technology Department, and is sponsored by the YPG, Shaanxi Coal Group, and Shaangu Manufacturing Group. This industrial support complements the expertise and experience of the Shaanxi/Wyoming Partnership, and provides additional technical abilities essential to constructing commercial-scale storage facilities. Industrial and governmental support are required to supply additional expertise and financial support to design and construct the compression, pipeline, and injection facilities needed for field demonstration projects. The Shaanxi/Wyoming Partnership was expanded during the CERC's first phase to include expertise from the Los Alamos National Laboratory, the Rock and Soil Mechanic Institute of the Chinese Academy of Sciences, the Huaneng Clean Energy Research Institute, and Lawrence Livermore National Laboratory. A high-priority objective of the partnership is to store commercial quantities of anthropogenic CO_2 safely and permanently in the Ordovician Majiagou Limestone in the Ordos Basin, northern Shaanxi Province, China and in the Mississippi Madison Limestone in the RSU, Wyoming.

During the previous five years, there have been 5 field trips to the Ordos Basin and 7 trips to Wyoming basins jointly taken by the U.S. and Chinese CERC-ACTC partners. The Governor of Wyoming, President of Wyoming Senate, Wyoming senators and representatives, professors and research scientists have visited coal convention and CO_2 capture facilities in the Ordos Basin. Shaanxi and Shanxi governors, department heads, general managers of YPG, ShaanGuo, Shaaanxi Coal Group, Huabei Oil Field, professors and research scientist have visited CCUS and CO_2-EOR projects in Wyoming. Five research scientists from SPIERCE worked on the joint CCUS research project at UW from 2 weeks to over one year. Three research scientists from UW worked with Chinese partners in the SPIERCE and YPG labs to analyze and interpret geological data, generate reservoir models, and conduct injection numerical simulations. The close partnership and productive cooperation provide great opportunities to share knowledge and experiences on the development of a sustainable low carbon economy.

Field trips

- A field trip to the Wyoming Laramide basins (April 2012), which was attended by the Chinese CERC team members, produced highly productive discussions about information transfer and the design of cooperative projects in both Wyoming and Shaanxi. The field observations convinced the CERC-ACTC partners that the Lance Formation and Madison Limestone in Wyoming serve as instructive analogs to the Yanchang Formation and Majiagou Limestone in the Ordos Basin. Both CMI and its Chinese partners were enthusiastic about sharing their expertise and experience in characterizing the CCUS attributes of the most promising CO_2 storage sites in Wyoming and Shaanxi.
- A field trip was conducted to the Ordos Basin (June 2012) and included visiting a CO_2 capture plant in the Yulin to evaluate the availability of CO_2 resources for EOR. A facility that is capable of capturing 5 mt of CO_2 (concentration greater than 99%) was installed at the Yuheng Coal Chemical Plant. The main purpose of this field trip was to investigate the similarities and differences of the Majagou Formation and the Madison Limestone.
- A field trip to a CO_2-EOR project in Wyoming (August 2012) included officials from SINOPEC Huabei Oil Field delegation. The team visited the Wyoming Beaver Creek CO_2-EOR project to learn the processing and challenges of enhanced oil recovery using CO_2 flooding in the Madison.
- Field trip to the Ordos Basin (May 2013). Traveling to Jinbian Oil Field, Dinbian Oil Field, Wuqi Oil Filed, Yongning Oil Filed, and Xikou Oil Field to learn the reservoir characteristics for each field; discussion with field managers,

geologists, engineers about opportunities and challenges of integrated CO_2-EOR and storage in the natural oil reservoirs.

- Field trip to the CO_2-EOR project in Wyoming (August 2013). Yanchang delegation and the UW team visited the Wyoming Grieve CO_2-EOR project to learn the processing and challenges of enhanced oil recovery using CO_2 flooding.
- Field trip to the Ordos Basin (September 2013). The field work in the Ordos Basin greatly improves the CMI team members understanding of both the Majiagou and Yanchang formations. The outcrops of potential saline aquifers and CO_2-EOR reservoirs were studied. Both CMI and its Chinese partners are enthusiastic about sharing their expertise and experience in characterizing the CCUS attributes of the most promising CO_2 storage sites in Wyoming and Shaanxi.
- A field trip to Wyoming Green River Basins (November 2013), which were well-received by the Chinese CERC-ACTC team members, produced highly productive discussions about the CCUS experience and share the design of cooperative projects in both Wyoming and Shaanxi. After the field trip, three research scientists from the NWU continued to work in Laramie at CMI on the following assignments: 1) assemble information regarding the regional geology, structural/stratigraphic framework, and thermal/burial history of the Ordos Basin, and assess the availability of public-domain data; 2) inventory the distribution of energy resources in the Ordos Basin, including oil, gas, and coal; and 3) delineate potential CO_2 sources in the Ordos Basin. Accomplishing these three tasks significantly expedited achievement of a better understanding of CCUS for both nations.
- A field trip (February 2015) to the Huaneng CCUS demonstration project in Bohai Bay and Yanchang Integrated Coal/Petroleum Chemical Industry Park in the Ordos Basin to investigate the opportunities of integrated CO_2 storage with CO_2-EOR and EWR.

Acknowledgements

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CO_2-EOR and Geological Storage

Joint Project

U.S. Research Team Lead

- **University of Wyoming**

China Research Team Lead

- **Shaanxi Provincial Institute of Energy Resources and Chemical Engineering**
- **Rock and Soil Mechanic Institute, Chinese Academy of Sciences**

China Partners

- **Yanchang Petroleum Group Research Institute**

Overview

The overlapping development of relatively new coal conversion industries with existing oil and gas industries in the Ordos Basin, China, has created unique opportunities to apply a systematic approach to development in Wyoming: an integration of geological CO_2 storage and enhanced oil recovery using CO_2 flooding (CO_2-EOR). The enhanced oil recovery via CO_2 flooding (CO_2-EOR) is a widely accepted and effective recovery technique that the oil industry has used for decades. In the U.S., CO_2-EOR projects in Wyoming and Texas have demonstrated that CO_2-EOR techniques can routinely increase oil recovery by 5 to 20 percent, depending on reservoir conditions and applied technology. Concurrent with stranded oil recovery, about one-third of the injected CO_2 remains in the subsurface during the CO_2-EOR process, while about two-thirds is recycled and recompressed for injection back into the reservoir. At the completion of CO_2-EOR projects, all CO_2 used for flooding is permanently stored in the depleted oil fields. The integration of geological CO_2 storage with enhanced oil recovery will increase oil and gas production, reduce CO_2 storage costs, and improve environmental protection.

The Ordos Basin of China is rich in energy resources: the basin is ranked first in China for coal, coalbed methane, and natural gas production, and fourth in oil production. The coal deposits in the Ordos Basin account for 39% of total Chinese coal resources (3.98 trillion tonnes). Mature oil fields in the Ordos Basin are excellent candidates for enhanced oil recovery via CO_2 flooding. Additionally, overlapping development of relatively new coal conversion industries with existing oil and gas industries in northern Shaanxi Province has created a unique opportunity to integrate geological CO_2 storage with CO_2-EOR.

Applying experience gained during CO_2-EOR and CCUS projects in Wyoming, researchers at the University of Wyoming Carbon Management Institute (UW CMI) are working closely with scientists from Northwest University (NWU), the Shaanxi Provincial Institute of Energy Resources and Chemical Engineering (SPIERCE), and the Yanchang Petroleum Group (YPG) to expedite CO_2-EOR and geological CO_2 storage projects in the Ordos Basin. Presently, many CCUS projects focus on capture and storage of CO_2 from coal-fired power plants. Higher energy consumption/penalty and costs of CO_2 capture from coal-fired power plants have become serious technical and financial obstacles for commercial-scale CCUS and CO_2-EOR projects. In Northern Shaanxi Province, the coal conversion industry (i.e., coal to methanol, coal to olefins, etc.) provides affordable, capture-ready CO_2. Compared with other CCUS projects, the ability to use CO_2 from the coal conversion industry for CO_2-EOR and geological CO_2 storage make these projects in the Ordos Basin more cost-effective and technologically efficient.

Oil fields in the Ordos Basin are being screened and prioritized based on CO_2-EOR criteria and proximity to CO_2 sources (i.e., coal conversion plants). Targeted high-priority candidates will be investigated further. Compared with the CO_2-EOR projects in the Texas and New Mexico Permian Basin and Wyoming Green River, Powder River and Wind River basins, the biggest challenge for CO_2-EOR projects in Northern Shaanxi Province is the development of advanced technology to deal with anomalously low-pressured reservoirs that are characterized by very low porosity and permeability, and high heterogeneity. Three-dimensional reservoir characterization, CO_2-EOR potential screening, geological storage reservoir modeling and injection numerical simulations, systematic performance assessments, and economic evaluations have been used to select sites for EOR/CO_2 storage demonstration projects.

Research Objectives

Applying experience gained from CCUS and CO_2-EOR projects in Wyoming, CMI, located in the School of Energy Resources at the University of Wyoming worked closely with SPIERCE, YPG, and NWU to develop a demonstration project that combines enhanced oil recovery using CO_2 with geological CO_2 storage. The availability in the Ordos Basin of large quantities of nearly pure CO_2 associated with the coal-to-chemical industries greatly facilitate potential CO_2 tertiary recovery projects. Two major goals of the proposed demonstration project are: 1) utilization of CO_2 from the coal-to-chemical facilities to support CO_2-EOR projects in the Ordos Basin, and 2) integration of CO_2-EOR projects with commercial CO_2 storage projects.

The goal of Subtask 6.2 is to build the scientific, technological, and engineering framework necessary for CO_2 utilization via enhanced oil recovery (EOR) in conjunction with safe, permanent storage of large quantities of anthropogenic CO_2 in the Ordos Basin in China and Laramide basins in Wyoming. The project goals for this subtask will be achieved by accomplishing the following tasks:

- Evaluating the geological characteristics of potential CO_2-EOR reservoirs in the Ordos Basin;
- Comparing the reservoir characteristics of mature oil fields in the Ordos Basin with Wyoming CO_2-EOR reservoirs;
- Constructing detailed 3-D geological models of the targeted oil reservoir;
- Numerically simulating CO_2-EOR performance for a variety of EOR scenarios at the selected depleted oil fields; and
- Evaluating the feasibility of combining CO_2-EOR with CO_2 storage.

Summary of Research Activities

SUMMARY OF TASKS

Lessons learned from current U.S. CO_2-EOR projects

Over the past 40 years, CO_2 flooding has become a mature technology capable of effectively enhancing oil recovery in mature and mostly-depleted oil reservoirs. Particularly, CO_2 flooding improves the efficiency of oil recovery significantly compared with primary (pressure depletion) and secondary (water flooding) recovery methods (Oil and Gas Journal, 2012, Manrique et al, 2010).

Production from 120 individual U.S. CO_2-EOR projects during 2012 averaged 352,221 barrels of oil per day (BOPD; O&G Journal, 2012), or approximately 6% of the total U.S. crude oil production of 6 million BOPD. Of the CO_2-EOR production, 308,564 BOPD is from CO_2 miscible flooding, and 43,657 BOPD is from CO_2 immiscible flooding. CO_2 flooding technology has surpassed thermal technology (steam, in-situ combustion, and hot water) as the most commonly used method of enhanced oil recovery in tertiary basins (Figure 1).

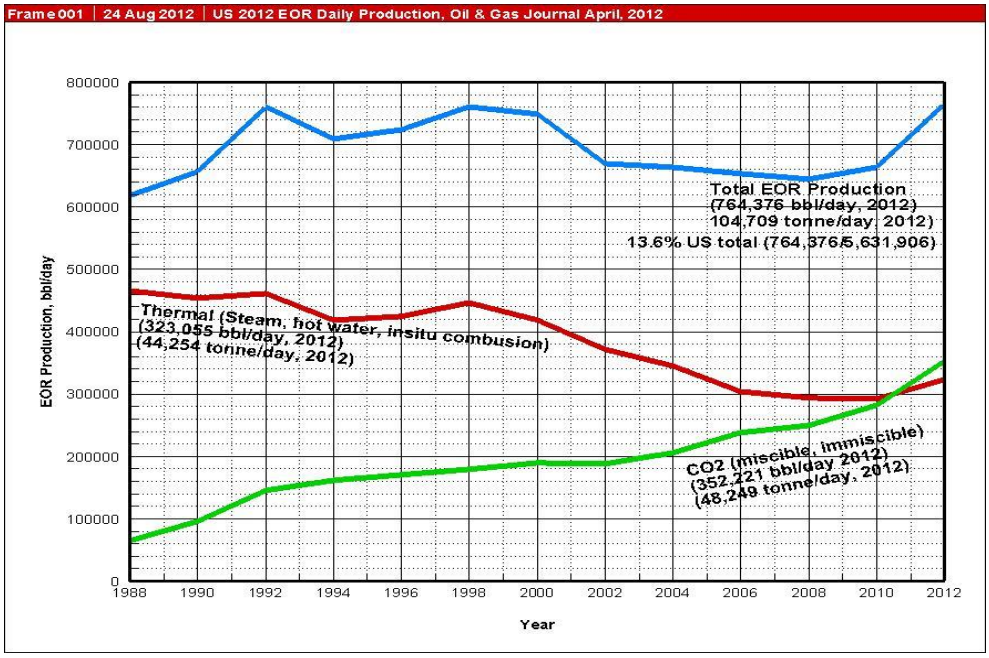

Figure 28: Plot of U.S. EOR production from 1988 to 2012. The blue line shows total EOR production; the red line shows thermal EOR production, and the green line indicates CO_2-EOR production. The CO_2 flooding technology surpassed thermal technologies (i.e., steam, in-situ combustion, and hot water) becoming the most commonly used method for enhanced oil recovery projects.

Miscible CO_2 flooding has achieved widespread uses in the southwest, mainly in the Permian Basin, Rocky Mountain, and Mid-Continent regions of the U.S. Including some additional EOR production in Alaska partly related to CO_2 injection. The oil and gas industry generally handles CO_2 in its supercritical phase, which is stable above the critical point of 6.9 MPa (1087 psi) and 31 °C (88 °F). In supercritical state, injected CO_2 in a reservoir behaves as a liquid with respect to density, and like a gas with respect to viscosity. Under suitable reservoir pressure and oil

compositions, injected CO_2 could mix thoroughly with the crude oil within the reservoir, resulting in the oil volume increase through oil swelling and the subsequent reduction of oil viscosity, eliminate interfacial tension between the oil and CO_2, and the reduction of the capillary forces that inhibit oil flow through the pores of the reservoir (Brock et al., 1989, Shtepani, 2007, Manrique et al., 2010). Theoretically, all contacted oil could be recovered under CO_2 miscible flooding (Shtepani 2007), although in the U.S. CO_2 flooding projects recovery is usually limited to about 5 to 22% of original oil in place (OOIP). The CO_2 flooding efficiency is affected by a number of parameters, including reservoir residual pressure, residual oil saturation, oil composition, viscosity, reservoir porosity and permeability, sedimentary architecture especially reservoir heterogeneity and natural fractures.

Based on years of experience in laboratory, field pilot and demonstration tests, and full-scale commercial operations, numerous miscible CO_2 enhanced oil recovery screening criteria has been suggested by several investigators (Brashear and Kuuskraa, 1978; Goodlett, et al., 1986; Taber, et al. 1997; Klins, 1984; Taber, and Martin, 1983; DOE, 2010; Brock et al., 1989, Manrique et al., 2010). CO_2 flooding has been successfully applied to both sandstone and carbonate reservoirs. Homogenous reservoir, well-collect thin beds are preferred for a CO_2 EOR project. For an optimized miscible CO_2 project, recommended crude oil gravity should be higher than 22 API, with current projects ranging from 27 to 44 API. Recommended viscosity is less than 10 cp, with current projects ranging from 0.3 to 6 cp. Residual oil saturation is recommended above 40%, with oil saturation for current projects ranging from 15 to 70%. The high percentage of intermediate compositions (C5 to C12) in crude oil is also favorable for the miscible CO_2 flooding. Residual reservoir pressure is a critical parameter for a CO_2 flooding project. Many projects inject water to establish reservoir pressure before CO_2 flooding. Residual reservoir pressure must be larger than minimum miscible pressure, which is often represented by reservoir depth. Current project depths range from 2500 ft to over 11,250 ft (Peterson et al., 2012). The reservoir temperature is not a critical screening criterion, but the higher temperature could increase the expandability of the crude oil. Porosity values vary widely in different depositional systems but generally range from 6 to 30% (Beike and Holtz, 1996). The type of porosity and architecture also is important. Well-connected porosity of similar size is the best type for CO_2-EOR miscibility projects. Permeability determines the fluid dynamics in a reservoir. High permeability will allow high volumes of CO_2 to be injected into a single well, thus reducing cost. Homogenous, high permeability will also allow CO_2 to move more quickly into the reservoir and increase sweeping efficiency.

The reservoir heterogeneity and natural fractures can be a potential contributor to an unsuccessful CO_2 flooding project, especially in depositional systems having high vertical and horizontal variabilities in permeability. Strata that have high values of permeability could form an unstable flow (viscous fingering) resulting in CO_2 having an early breakthrough, reducing oil-sweep efficiency. To prevent the occurrences of unstable flow and to reduce the amount of CO_2 that is needed for injection, CO_2 is typically injected into the reservoir alternately with water (WAG) since water sweeps through the reservoir more uniformly. The WAG can significantly reduce viscous fingering and allow CO_2 flow through the reservoir after full miscibility is achieved.

Integrated Energy/CCUS development strategy

CMI in the School of Energy Resources at University of Wyoming has developed an integrated energy/CCUS development strategy (Figure 2, Surdam et al., 2011), which aims to synchronously and systematically develop coal mining, coal conversion industry, coalbed methane production (CBM), CO_2 enhanced oil recovery, and CO_2 storage in the Powder River Basin, Wyoming (Figure 3).

In this systematic approach strategy, by-products and problems associated with the development of one resource become

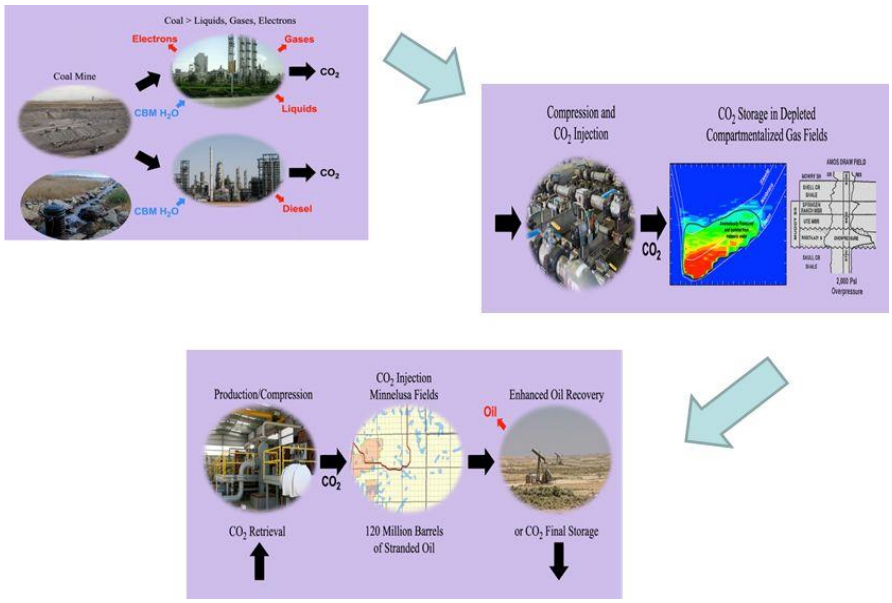

Figure 29: An integrate energy development strategy includes (1) development of coal mining; (2) the new coal-to-chemical facilities; (3) water produced with coal bed methane production is used to support the coal-to-chemical industries; (4) the depleted gas fields and saline aquifers would initially be used as anthropogenic CO_2 (emitted from coal-to-chemical plants) surge tanks to support EOR activities.

part of a useful resource for the development of another. This integrated energy development strategy includes one in which (1) coal mines continue to use existing extractive technologies or newly developed improved technologies; (2) new coal-to-chemical facilities can be located as close to mines as possible; (3) water production from coal bed methane extraction can be monetized and used to support the coal-to-chemical industries; and (4) the depleted gas fields and saline aquifers could initially be used as anthropogenic CO_2 (emitted from coal-to-chemical plants) surge tanks to support EOR activities. Following this, as stranded oil in nearby oil fields is recovered, depleted gas fields could be used for more permanent CO_2 storage. Using initial storage sites as a surge tank would allow adjacent EOR projects in mature fields to have optimal flexibility in designing variable injection rates and in alternating water and CO_2 injection (WAG) strategies; and (5) CO_2 stored in the surge tanks can be used to enhance oil recovery.

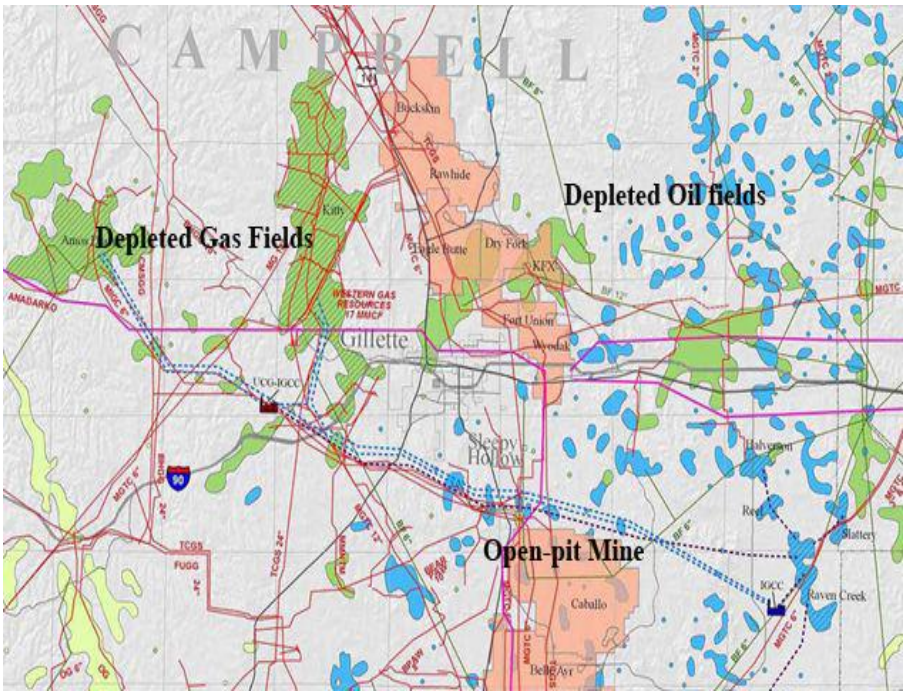

Figure 30: Map showing the distribution of open-pit mines, depleted gas fields, and depleted oil fields near the Gillette City, Powder River Basin, Wyoming, where is an ideal situation for applying integrated energy/CCUS development strategy.

The Ordos Basin has a very similar geological setting and energy resources profile comparing to the Powder River Basin (Figure 3). The overlapping development of relatively new coal conversion industries with existing oil and gas industries in northern Shaanxi Province has created a unique opportunity for applying the systematic approach strategy developed in Wyoming: the integration of geological CO_2 storage and CO2-EOR. The coal conversion industry (i.e., coal to methanol, coal to olefins, etc.) provides affordable, captured-ready CO_2 sources for developing large-scale CO_2-EOR and storage projects in the Ordos Basin, China. Compared with other CCUS projects, the ability to use CO_2 from the coal-conversion industry for CO_2-EOR and geological CO_2 storage will make these projects in the Ordos Basin more cost effective and technologically efficient.

An integrated energy development strategy has been created for the Shanbei National Energy Base. This integrated energy development strategy aims to synchronously, systematically develop coal mining, coal conversion industry, coalbed methane production (CBM), CO_2 enhanced oil recovery, and CO_2 storage in the Shanbei National Energy Base. Again, systematic approach strategy, problems associated with the development of one resource becomes part of a useful resource for the development of another. First, coal mining would continue using existing extractive technology, or improved technology. Secondly, the new coal-to-chemical facilities could be located as close to the mines as possible. In the Ordos Basin, recently constructed coal-to-chemical plants and associated coal mines are sited in the same location – over underground coal mines (i.e., Shenmu Jinjie Industry Park and Yanchang Jinbian Industry Park). Next, coalbed-methane produced water would best support these coal conversion facilities. The volume of water required to supply the plants will vary depending on facility specifications. In the Ordos Basin, the coal-to-methanol plants are designed based on a 6:1 ratio of water to products. A 0.6 million tons of methanol plant in the Ordos Basin annually uses 1.8 million tons of coal and 6.0 Mt of water and emits 4.0 million tons of CO_2. A seven-million-barrel diesel plant annually uses 3.5 million tons of coal and approximately 56 million tons of water and emits 2 million tons of CO_2. Presently, coal conversion industries in the Ordos Basin generate 8 million tons of methanol and 0.76 million tonnes of diesel annually, emit 46 million tons of CO_2. This ready-captured, high concentration CO_2 could be stored in the adjacent depleted oil and gas fields, and/or saline aquifers, the Majiagou reservoir. The Majiagou reservoir has a tremendous CO_2 storage capacity. Furthermore, Liao et al. (2012) has assessed the CO_2 storage capacities of 14 oil fields in the Ordos Basin. The total storage capacity of these 14 depleted oil fields is estimated as high as 100 million tonnes. These depleted oil fields are ideal locations for 1) storage sites for CO_2 emitted by coal conversion facilities, and 2) sources of CO_2 for EOR projects in adjacent depleted Yanchang reservoirs (Figure 4). The Majiagou reservoirs and depleted oil/gas fields would initially be used as CO_2

surge tanks to support EOR activities. When the stranded oil in the Yanchang reservoirs is recovered, the depleted oil fields could be used for more permanent CO_2 storage. Using the initial storage site as a surge tank would allow adjacent EOR projects in the Yanchang reservoirs to have optimal flexibility in designing variable injection rates and in alternating water and CO_2 injection (WAG) strategies.

As shown in Figure 4, more than 40 mature Yanchang oil fields with EOR potential are located near the previously described resource confluence and are eligible for recovery via CO_2 flooding. Many have gone through the secondary recovery water flooding stage and appear ideal for CO_2 miscible flooding. These Yanchang oil fields together contained 2 billion tonnes of original oil in place (OOIP, Wang et al., 2007). Typically, CO2 flooding recovers at least 10% additional production, or in the case of the Yanchang oil fields, 200 million tonnes of oil. Recovering the stranded oil via CO_2 flooding would require 700 million tonnes of CO_2 (3.5 tonnes per tonne of incremental oil recovered). If the EOR project lasted 30 years, about 23 million tonnes of CO_2 would be required annually for the CO_2-EOR projects in the Ordos Basin. Current coal conversion facilities (46 million tons of CO_2 emitted annually) would more than adequately support EOR activities. Importantly, CO_2 used for the EOR projects would be monetized. A very conservative estimate suggests that CO_2 would be worth $40/tonne, or $28 billion to recover the 200 million tonnes of stranded oil in the Yanchang reservoirs. Therefore, the CO_2 typically regarded as a problem with respect to sequestration is worth approximately $28 billion in this scenario. Moreover, the Yanchang reservoirs from which the stranded oil is recovered could be converted to permanent storage sites for CO_2, doubling the CO_2 storage capacity available for the coal conversion facilities. Instead of 200 million tonnes of CO_2 storage capacity at the end of EOR operations, there would be 400 million tonnes.

CO_2-EOR potential and challenge in the Ordos Basin

The Ordos Basin is rich in energy resources similar to Powder River Basin in Wyoming. The energy/environment development strategy developed in the Wyoming Powder River Basin is very much applicable to the Ordos Basin. At present, most CCUS projects focus on capturing and storing CO_2 from coal-fired power plants. The greater energy consumption and higher cost of CO_2 capture from coal-fired power plants have become serious obstacles to commercial-scale CCUS and CO_2-EOR projects. The most prominent regional overlap of the coal-to-chemical and oil and gas industries occurs in Shaanxi Province (Figure 4), and availability of large quantities of nearly pure CO_2 associated with the coal-to-chemical industries has created an ideal environment to integrate CO_2 enhanced oil recovery with geological CO_2 storage in the Ordos Basin. Integrating these two critical energy development elements will increase oil and gas production and significantly reduce anthropogenic CO_2 emissions in an important energy-producing region of China.

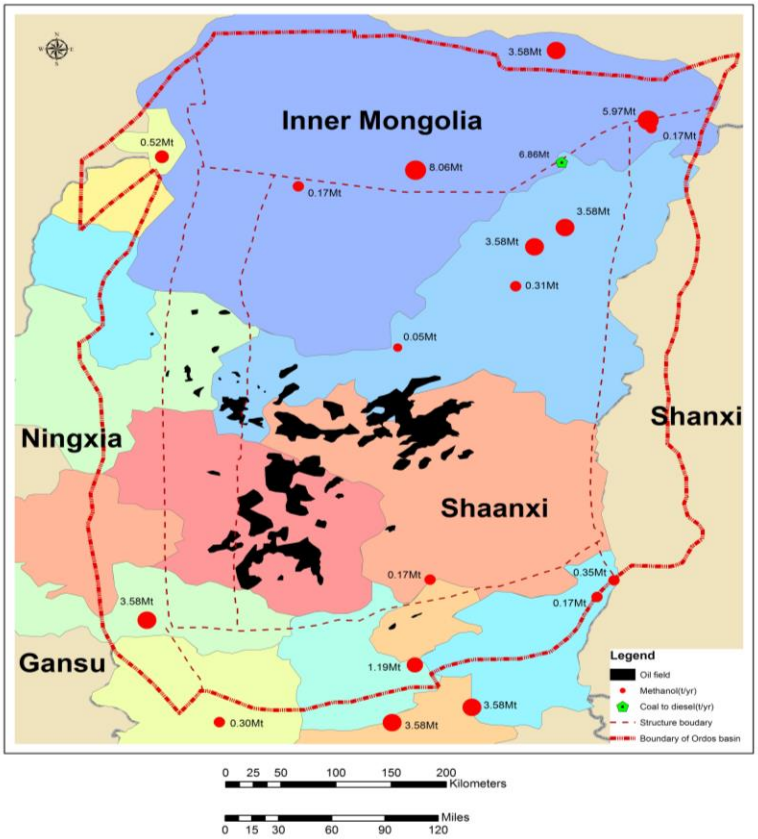

Figure 31: Map of the Ordos Basin showing geospatial districts, the location of gas and oil accumulations, and location of stationary CO_2 emission sources. The point source of CO_2 emissions is subdivided according to the industrial sector. The total annual CO_2 emissions in the Ordos Basin are approximately 400 Mt.

The majority of oil production in the Ordos Basin is from the Triassic Yanchang Formation. The interbedding lenticular sandstone, siltstone, mudstone, and shale was accumulated in the fluvial, delta, and lacustrine depositional environments. The Triassic Yanchang reservoirs are characterized by extremely low porosity, low permeability, low oil saturation, anomalously low reservoir pressure, and high heterogeneity. These characteristics directly resulted in a very low recovery (less than 15%) for the majority oil fields in the basin. Most fields are already in their later or middle development stage. Table 1 shows reservoir and crude oil properties for selected Yanchang reservoirs.

The depths of selected reservoirs range from 150 to 2200 meters, the thickness of individual sandstones range from 7 to 15 meters, porosity ranges from 8 to 17%, and permeability from 0.5 to 38 md (but can be less than 1 md). The formation

Table 4: Reservoir and crude oil properties for selected oil reservoirs in the Ordos Basin, China

Table 1. Reservoir and crude oil properties for selected oil reservois in the Ordos Basin, China															
Oil field	Depth meter	Reservoir	Bed Thinck. meter	Specific Gravity	API	Viscosity mPa.s	Pressure Mpa	Temp. C	Porosity %	Perm. md	Oil Satura %	Oil Type	Water type	TDS mg/l	MMP Mpa
YC	200-250	Chang 6	13	0.84	37	4.9	1.8	19	9.9	0.55		light/mediate	$CaCl_2$	10000	
YP	400-450	Chang 2	7.6	0.85	35	5.5	3.6	23	13	6.5		light/mediate	$CaCl_2$	46000	
ZC	400-450	Chang 6	7.6	0.84	37	5.5	3.6	23	11.2	1.65	53.6	light/mediate	$CaCl_2$	42400-87600	
QH	400-450	Chang 2	8.7	0.84	37	6.3	3.6	23	14	15		light/mediate	$CaCl_2$		
YD	350-550	Chang 6	15.7	0.84	37	6.3	4	24	9.4	0.5	51	light/mediate	$CaCl_2$		
GG	150-350	Chang 6	16	0.83	39	3.9	2	20	9.5	0.54	50.3	light/mediate	$CaCl_2$	10000	
ZY	150-350	Chang 6	14.5	0.85	35	3.5	2	20	9.2	0.3	56	light/mediate	$CaCl_2$		
ZL	600-800	Chang 2	5--18	0.85	35	8.9	7	32	17	7.3	42	light/mediate	$CaCl_2$	50000-70000	
TJ	600	Chang 2	14.8	0.84	37	4.6		29	17.6	38.2		light/mediate	$CaCl_2$		
PQ	1000	Chang 2, 4+5, 6	9.9	0.86	33	4.45-7.83	9	41	11	2.8	55	light/mediate	$CaCl_2$		
QY	1000	Chang 6	12	0.84	37	3.92	9	41	13.5	1.6	55.6	light/mediate	$CaCl_2$		
HS	1100	Chang 6	9.8	0.845	36	5.42	10	44	13.7	2.5	56	light/mediate	$CaCl_2$		
XH	1200	Chang 6	6.7	0.85	35	5	11	47	12	2.5		light/mediate	$CaCl_3$		
HU	1800		12	0.77	52	1.64	18	71.6	10	0.5		light/mediate	$CaCl_2$		19.5
MU	2200		14	0.73	62	1.35	22	76	8	0.5		light/mediate	$CaCl_2$		19.8
												light/mediate			
DB	2000	Chang 6	12	0.78	50	2	12	44	8	1	40	light/mediate	$CaCl_2$	70000	15.7

water type is calcium chloride with high total dissolved solid from 10,000 to 70,000 ppm. Reservoir pressure was regionally under-pressured, even at the beginning of the field development. The quality of crude oil is night or intermediate, with specific gravity ranging from 0.72 to 0.84 or API 35 to 62. The majority of reservoirs have oil saturations from 40 to 60%. Because all reservoir sandstones were deposited in fluvial and lacustrine environments, very low continuity and high heterogeneity is common for most reservoirs. The multi-age natural fractures were found in most cores from the Yanchang reservoirs. Figure 5 shows a typical distribution of the Yanchang pay zone in the Ordos Basin. The light and dark green areas are the compartmentalized, disconnected, lenticular sandstones and siltstones that are separated by mudstones

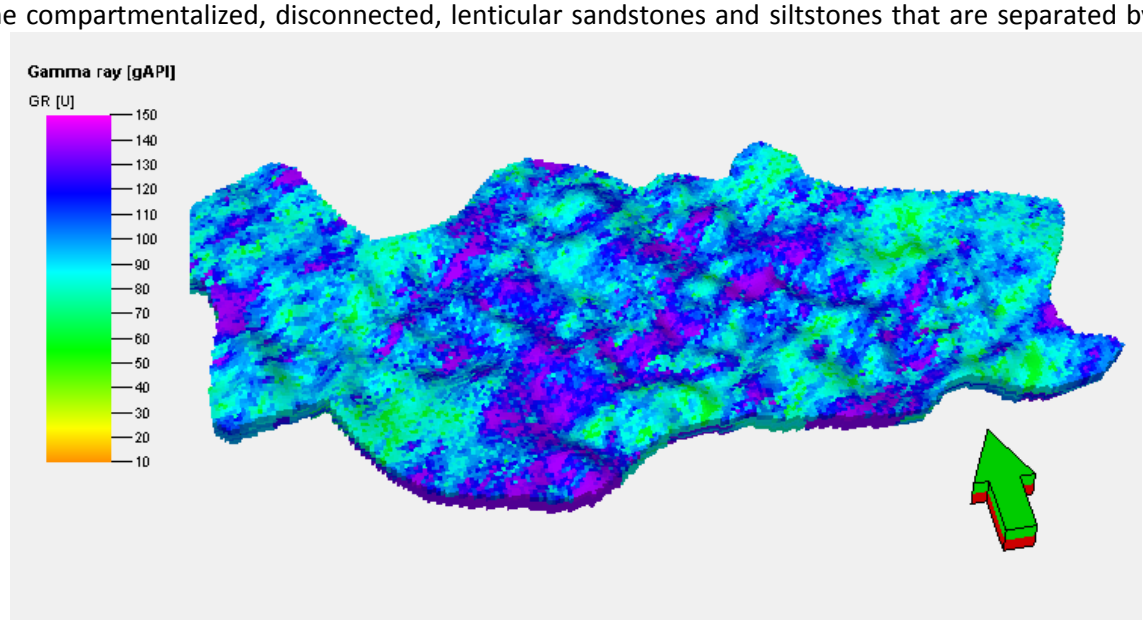

Figure 32: A typical Triassic Yanchang reservoir in the Ordos Basin shows the distribution of the compartmentalized, disconnected lenticular sandstone and siltstone (green color areas) is separated by mudstones and shales.

and shales. Multi series/direction fracture systems make the reservoir heterogeneity more severe (Figure 5).

The extremely low porosity, low permeability, low oil saturation, anomalously low pressured reservoir, and high reservoir heterogeneity make using CO_2 for enhanced oil recovery more challenging any CO_2-EOR projects in the U.S. This unique characteristic is one of major reasons why a CO_2-EOR project is not widely developed in the Ordos Basin, in spite of easily available high concentration CO_2 sources (from coal conversion plans). Table 2 lists the reservoir and crude oil properties for selected oil reservoirs in the Ordos Basin. Depths of selected reservoirs range from 200 meters to 2200 meters. Individual bed thickness in the pay zone ranges from 5 to 18 meters, and the crude oil is light oil or intermediates oil with specific gravity ranging from 0.73 to 0.86 (33 – 62 API) and a viscosity ranging from 1.3 to 9 mPa. All reservoirs were

anomalously underpressured with pressure coefficient of 0.9 (0.39 psi/ft). Therefore, residual pressures for most candidate reservoirs are below the minimum miscible pressures. Most reservoirs are characterized by low porosity and permeability, and selected reservoirs range from 8 to 17%, with permeability from 0.5 to 38 md.

Table 5: Comparison of Ordos reservoir/crude oil properties with the U.S. CO_2 EOR Screening Guideline

	U.S. Recommended	U.S. Current Projects Range	Ordos
Gravity	< 0.92 (> 22 API)	0.81–0.89 (27-44 API)	0.73–0.86 (33-62 API)
Viscosity	< 10 cp	0.3–6 cp	1.3–9 cp
Composition	High C5 to C12 percent	Light–intermediates	Light–intermediates
Oil Saturation	> 40%	15%–70%	40%–56%
Formation	Thin beds	Sandstone/carbonate	Thin sandstone beds
Porosity	> 8%	4%–18%	5%–17%
Permeability	Not critical	3–31 md	0.1–7 md
Depth	> 800m (2600ft)		200–2500m (650–8200ft)

Table 2 compares reservoir and crude oil properties with the current U.S. CO_2-EOR screening guidelines (Assembling from literature; especially Taber et al., 1997; Shtepani, 2007; and Lake et al., 2008). From these comparison, gravity, viscosity, crude oil composition, and formation type of the Ordos reservoirs all favor CO_2 miscible flooding. Major challenges come from anomalously low reservoir pressure, low porosity, and higher reservoir heterogeneity. Low permeability may help to increase CO_2–oil multiple contact chance, but also may be an issue for reaching sufficient flow rates.

Even though a CO_2-EOR project in the Ordos Basin faces more challenges, many favorable conditions for developing the CO_2-EOR projects in the Ordos Basin are noted. Besides availability of local CO_2 sources, thin compartmentalized beds are favorable to create a stable flow (reduce the CO_2 flow figuring) and increase sweep efficiency. Reservoir pressure is one of the most important factors to determine CO_2 miscibility in oil recovery. According to Klins and Bardon (1991) and Shtepani (2007), it is possible to achieve different levels of miscibilities, ranging from immiscible (low-pressure reservoirs) through intermediate- to high-pressure applications (miscible displacement). Minimum miscibility pressure has a wide range of values depending on depth, temperature, and crude oil composition. A minimum of 8 MPa (800 meters, 1180 psi) is generally regarded as a target reservoir pressure at which to conduct a successful CO_2 flood. This condition imposes an important restriction related to the current level of reservoir pressure for a miscible CO_2 flooding. A significant number of reservoirs in the Ordos Basin fall below this level (Figure 6).

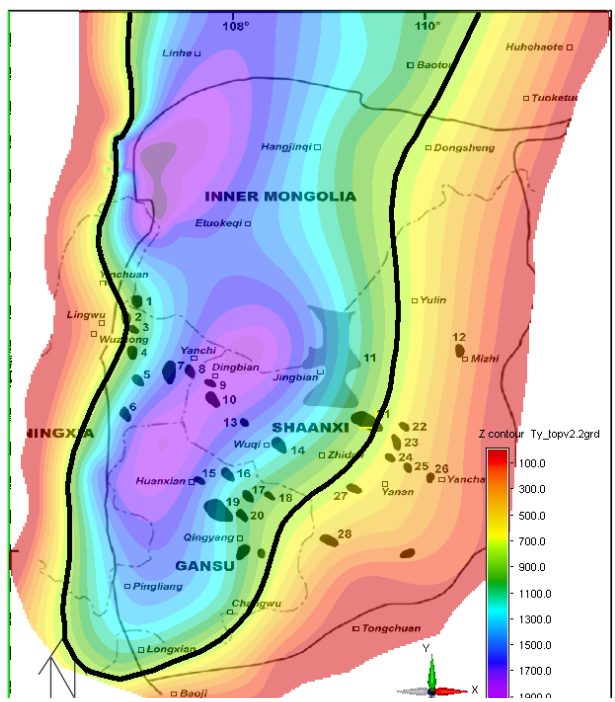

Figure 33: Yanchang Formation oil fields is overlapped on the map of burial depth of the Yanchang Formation top, which is main oil and gas production formation in the Ordos Basin.

Figure 6 shows oil fields overlapping burial depth of the Yanchang Formation top, which is main oil and gas production formation in the Ordos Basin. The dark-black line is 800-meter contour of the burial depth to top of Yanchang Formation. The depths of oil fields inside the dark-black line areas in the diagram (Figure 9) are at least 800 meters of present day depth. Since the oil and gas reservoirs in the Ordos Basin typically have very low percent of movable formation water, the water flooding is not efficient for the enhanced oil recovery. Injecting CO2 into the reservoir before production may be an efficient way to establish reservoir pressures to meet minimum miscible pressure requirement. A pre- CO_2 injection simulation for building the reservoir pressure has been generated for different scenarios. For the test reservoir, the average depth of the targeted is 1500 m with porosity 10% and permeability 1 md. The injection rate of supercritical CO_2 is 23 kg/minutes. The residual reservoir pressure is anomalously underpressured at

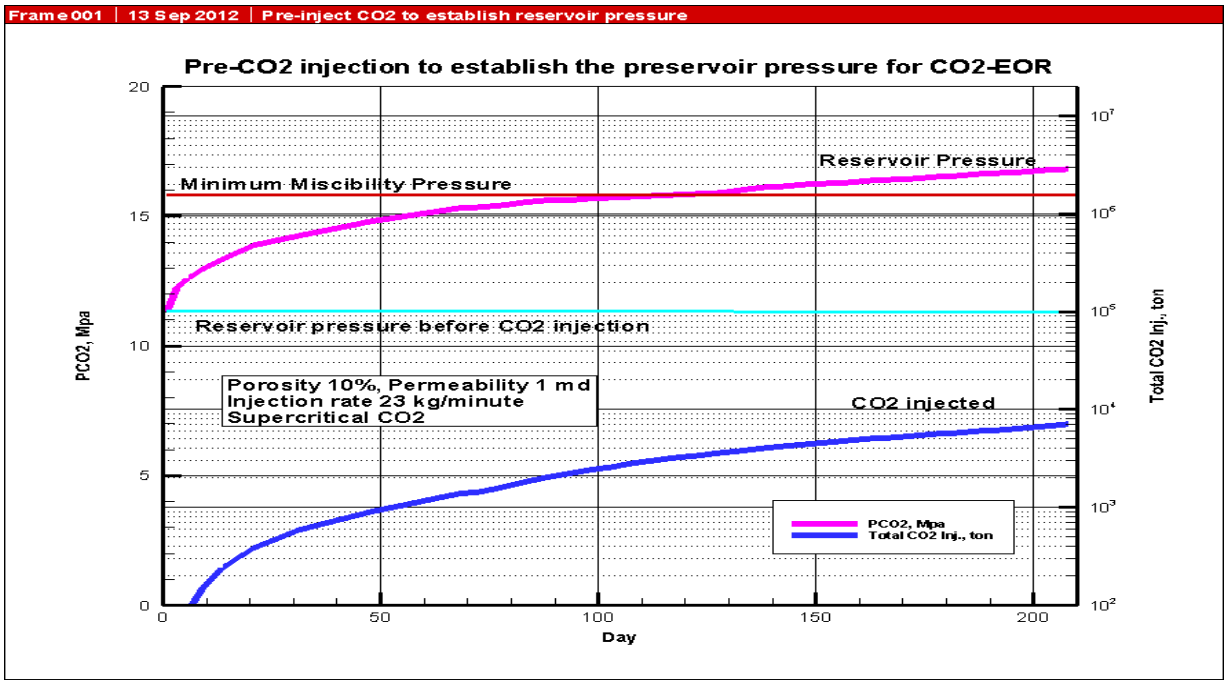

Figure 34: Plot the results of CO_2 injection simulation from LANL FEHM simulator shows injection rat and time needed to establish the minimum miscible pressure for a miscible CO_2 flooding project.

11.5 Mpa. Results from Los Alamos National Laboratory FEHM simulator show that minimum miscible pressure could established for this reservoir after 100 day's supercritical CO_2 injection (Figure 7).

MAJOR FINDINGS AND OUTCOMES

- An integrated energy/CCUS development strategy was created to systematically develop synchronous technologies of coal mining, coal conversion industry, coalbed methane production (CBM), CO_2 enhanced oil recovery, and CO_2 storage for the Ordos Basin, China and the Powder River Basin, Wyoming. In this systematic approach strategy, a contentious problem associated with the development of one resource becomes part of a useful resource for the development of another.
- The Ordos Basin has a very similar geological setting and energy resource profile compared to the Powder River Basin, Wyoming. Development of relatively new coal conversion industries with existing oil and gas industries in northern Shaanxi Province has created a unique opportunity for applying the systematic approach developed in Wyoming: the integration of geological CO_2 storage and CO_2-EOR and the coal conversion industry (i.e., coal to methanol, coal to olefins, etc.) provides an affordable, capture-ready CO_2 sources for developing large-scale CO_2-EOR and storage projects in the Ordos Basin. Compared with other CCUS projects, the ability to use CO_2 from the coal-conversion industry for CO_2-EOR and geological CO_2 storage will make the similar projects in the Ordos Basin more cost effective and technologically efficient.
- The majority of oil production in the Ordos Basin is from the Triassic Yanchang Formation. The Triassic Yanchang reservoirs are characterized by extremely low porosity, low permeability, low oil saturation, anomalously low reservoir pressure, and high heterogeneity. The integrated CO_2-EOR with storage project faces more challenges in these unconventional reservoirs in the Ordos Basin than any CO_2-EOR project in the U.S.
- Even though a CO_2-EOR project in the Ordos Basin faces more challenges, there are still favorable conditions for developing CO_2-EOR projects in the Ordos Basin. These include an abundance of local CO_2 resources, thin beds, compartmentalization, and light crude conditions that are favorable for creating a stable flow (reducing CO_2 viscos fingering) and increasing the sweep efficiency and mobility of the CO_2.

Major Achievements

Meetings and Presentations

- Attended the third advanced coal technology conference in Xian (June 2012). Surdam and Jiao presented a talk titled "Reservoir Simulation of CO_2 Storage on the RSU Based on a Robust Database and an Accurate Model of

Geological Heterogeneity". Jiao and Surdam also presented a talk titled "Integration of Enhanced Oil Recovery with CO_2 Storage in Mature Oil Fields of the Ordos Basin, China: Opportunities and Challenges".

- Attended the Eleventh Greenhouse Gas Control Technologies conference in Kyoto, Japan (November 2012). Two papers were presented at this conference. A feasibility study of the integration of enhanced oil recovery (CO_2 Flooding) with CO_2 storage in the mature oil fields of the Ordos Basin, China (Wand and Jiao); Characterizations of the CCUS attributes of a high-priority CO_2 storage site in Wyoming, U.S.A. (Surdam and Jiao).
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity was presented at the AAPG Annual Convention 2013, Pittsburgh.
- An oral presentation of the importance of CO_2 storage in designing strategies for the sustainable development of energy resources was presented at the Twelfth Annual Carbon Capture, Utilization & Sequestration Conference, 2013, Pittsburgh.
- An oral presentation focused on the 3-D permeability distribution of reservoir rocks in the subsurface in the RSU was presented at the Twelfth Annual Carbon Capture, Utilization & Sequestration Conference, 2013, Pittsburgh.
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity – the greatest uncertainty in numerically simulating CO_2 sequestration processes is characterizing geological heterogeneity in three dimensions, was presented at the Northwest University, Xian.
- An oral presentation that focused on the importance of CO_2 storage in designing strategies for the sustainable development of energy resources was presented at ShaanGu Power Company, Xian.
- An oral presentation of global warming and climate change – 45-million-year-old rocks in Wyoming support the concept was presented at the Shiyou University, Xian.
- An oral presentation of detailed CO_2 storage reservoir/site characterization: the key to optimizing performance and maximizing storage capacity was presented at the AAPG Annual Convention 2013, Pittsburgh.
- Attended the U.S. DOE – China NDRC first CCUS initiative workshop at Beijing (April 2014). During the workshop, organizations from both countries presented their cooperation on joint CCUS works to date, along with ongoing and planned activities. In the workshop, Jiao and Northam presented the outcome from the Wyoming and Ordos Basin CCUS projects.
- Attended GHGT 12 in Austin, Texas (November 2014): At the meeting, Jiao and Zhou presented the research results from a feasibility study of the geological CO_2 storage in the Ordos Basin. Luo and Zhou presented a paper titled "The Ordos Basin: A Premier Basin for Integrating Geological CO_2 Storage with Enhanced Oil Recovery Projects in China".
- Visited the Huaneng Clear Energy Research Institute, Shaanxi Provincial Institute of Energy Resources and Chemical Engineering, Yanchang Petroleum Group, Shaanxi Coal Group, and Changqing Petroleum Company (February 2015) to share the current CCUS project status, address the challenges, and discuss more collaboration opportunities. Highly productive discussions about information transfer and the design of potential cooperative projects for CERC-ACTC Phase II between Wyoming, Shaanxi, and Huaneng Clean Energy Research Institute were further finalized. A major point of these discussions was to promote an integrated CCUS demonstration project in China.
- During the second quarter, 2015, the School of Energy Resources at UW hosted three delegations of Chinese partners: the Shaanxi delegation, led by provincial Vice Governor Wang Lixia, the Shanxi delegation, led by provincial Governor Li Xiaopeng, and SPIERCE delegation, led by Director Zhou Lifa. During the visits, the current CCUS project status, challenges, and future collaboration opportunities were discussed. Discussions regarding broad cooperation opportunities in clean energy and low carbon economy developments, and the design of potential cooperative projects for CERC-ACTC Phase II between Wyoming, Shaanxi, and Huaneng Clean Energy Research Institute were further finalized. A main purpose of the discussions was to promote an integrated CCUS demonstration project in China.
- In the third quarter, 2015, the UW team attended three meetings, UW CO_2 Conference at Casper, Wyoming, DOE Carbon Storage R&D Project Review Meeting at Pittsburgh, and Fifth China (Taiyuan) International Energy Industry EXPO, Low Carbon Development Summit at Taiyuan, China. At the Low Carbon Development Summit, Mark Northam was the keynote speaker and gave a talk on "Wyoming's energy resources – challenges and opportunities", Jiao Zunsheng presented a talk on "CCUS technology is vital to a sustainable energy future – the UW WYCUSP and CERC projects review".
- In the fourth quarter, 2015, the UW team attended three meetings, CERC-ACTC annual meeting at Jackson Hole, Wyoming, fifth International Advanced Coal Technology Conference, and 2015 U.S.-China CCUS Xinjiang Workshop. At CERC-ACTC annual meeting, Dr. Jiao presented the results from the Theme 6 study, and briefed UW and its

partners on the objective and work plans of the Phase II CO2-EOR proposal to CERC-ACTC. At the fifth International Advanced Coal Technology Conference, Director Kipp Coddington gave a talk on the impacts of regulatory and policy decisions on markets and research and technology investment decisions. At the 2015 U.S.-China CCUS Xinjiang Workshop, Dr. Jiao hosted a business-to-business panel discussion focused on creating CCUS hubs and building open-access pipelines in Xinjiang and the necessity of enabling incentives and policy.

Workshops

- UW and Chinese CERC-ACTC partners organized a workshop at Xian (June 2012). The CERC teams from both countries presented their progress, challenges, and plans for the CCUS projects from Wyoming, Illinois, Ordos, and Qinshui Basins. UW and Chinese partners—SPIERCE and Yanchang Petroleum Group—presented the progress of the stationary anthropogenic CO_2 resource inventory, geological CO2 storage site characterization, and CO_2-EOR feasibility study in both the Wyoming basins and Ordos Basins.
- Attended the CERC-ACTC workshop held at Wuhan (May 2014). At the workshop, the CMI team presented the research results from both the Wyoming RSU geological CO_2 storage site characterization project and the feasibility study of the geological CO_2 storage in the Ordos Basin. Lessons learned, and challenges from current CCUS projects were exchanged between the U.S. and Chinese partners. During the workshop, the potential joint demonstration projects were also identified for the CERC-ACTC Phase II.

List of Publications

- Jiao Z., R. Bentley, Y. Ganshin, F. McLaughlin, and S. Quillinan, 2015, Sealing capacity investigations of the multiple confining layers at the Rock Springs Uplift geological CO_2 storage site, DOE Pittsburgh CO_2 Conference, 2015
- Jiao Z., L. Zhou, R. Gao, T. Luo, H. Wang, H. Wang, F. McLaughlin, R. Bentley, and S. Quillinan, 2014, Opportunity and challenge of integrated enhanced oil recovery using CO_2 flooding with geological CO_2 storage in the Ordos Basin, China: in proceeding of the 12th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 63 (2014), p. 7761-7771.
- Luo T., L. Zhou, Z. Jiao, Y. Bai and S. Wang, 2014, The Ordos Basin: a premier basin for integrating geological CO_2 storage with enhanced oil recovery project in China: in proceeding of the 12th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 63 (2014), p. 7772-7779.
- Jiao Z., R. Surdam C., 2013, Advances in estimating the geological CO_2 storage capacity of the Madison Limestone and Weber Sandstone in the Rock Springs Uplift by utilizing detailed 3-D reservoir characterization and geological uncertainty reduction: in Surdam edit, Geological CO2 storage characterization, Springer Publication, p. 191-232.
- Surdam R., Z. Jiao, Y. Ganshin, R. Bentley, and M. Garvia-Gonzalez, 2013, characterizations of the CCUS attributes of a high-priority CO_2 storage site in Wyoming, USA: in proceeding of the 11th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 37 (2013), p. 3911-3918.
- Wang Y., Z. Jiao, R. Surdam, L. Zhou, R. Gao, Y. Chen, T. Luo, and H. Wang, 2013, A feasibility study of the integration of enhanced oil recovery (CO_2 flooding) with CO_2 storage in the mature oil fields of the Ordos Basin, China: in proceeding of the 11th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 37 (2013), p. 6846-6853.
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- Jiao Z., R. Surdam, Y. Ganshin, R. Bentley, and M. Garvia-Gonzalez, 2012, Documented subsurface three-dimensional geological heterogeneity in the Weber/Tensleep sandstone and Madison Limestone: Wyoming's highest-priority CO_2/hydrocarbon storage and production reservoir: AAPG 2012 Annual Convention, Long Beach.
- Surdam C. R. Z. Jiao, Y. Ganshin, and R. Bentley, 2012, The Rock Springs Uplift: a premier CO_2 storage site in Wyoming: Carbon Management Technology Conference CMTC paper 151216.
- Deng H., P. Stauffer, Z. Dai, Z. Jiao, and R. Surdam, 2012, Simulation of industrial-scale CO_2 storage: multi-scale heterogeneity and its impacts on storage capacity, injectivity and leakage: International Journal of Greenhouse Gas Control 10 (2012), p. 397-418.
- Surdam R., Z. Jiao, Y. Ganshin, R. Bentley, and M. Garvia-Gonzalez, 2012, characterizations of the CCUS attributes of a high-priority CO_2 storage site in Wyoming, USA: in proceeding of the 11th Greenhouse Gas Control Technology Conference: Elsevier, Energy Procedia, v. 5 (2012), p. 1-8.

Collaboration

Field trips

- A field trip to the Wyoming Laramide basins (April 2012), which was attended by the Chinese CERC team members, produced highly productive discussions about information transfer and the design of cooperative projects in both Wyoming and Shaanxi. The field observations convinced the CERC-ACTC partners that the Lance Formation and Madison Limestone in Wyoming serve as instructive analogs to the Yanchang Formation and Majiagou Limestone in the Ordos Basin. Both CMI and its Chinese partners were enthusiastic about sharing their expertise and experience in characterizing the CCUS attributes of the most promising CO_2 storage sites in Wyoming and Shaanxi.
- A field trip was conducted to the Ordos Basin (June 2012) and included visiting a CO_2 capture plant in the Yulin to evaluate the availability of CO_2 resources for EOR. A facility that is capable of capturing 5 mt of CO_2 (concentration greater than 99%) was installed at the Yuheng Coal Chemical Plant. The main purpose of this field trip was to investigate the similarities and differences of the Majagou Formation and the Madison Limestone.
- A field trip to a CO_2-EOR project in Wyoming (August 2012) included officials from SINOPEC Huabei Oil Field delegation. The team visited the Wyoming Beaver Creek CO_2-EOR project to learn the processing and challenges of enhanced oil recovery using CO_2 flooding in the Madison.
- Field trip to the Ordos Basin (May 2013). Traveling to Jinbian Oil Field, Dinbian Oil Field, Wuqi Oil Filed, Yongning Oil Filed, and Xikou Oil Field to learn the reservoir characteristics for each field; discussion with field managers, geologists, engineers about opportunities and challenges of integrated CO2-EOR and storage in the natural oil reservoirs.
- Field trip to the CO_2-EOR project in Wyoming (August 2013). Yanchang delegation and the UW team visited the Wyoming Grieve CO_2-EOR project to learn the processing and challenges of enhanced oil recovery using CO_2 flooding.
- Field trip to the Ordos Basin (September 2013). The field work in the Ordos Basin greatly improves the CMI team members understanding of both the Majiagou and Yanchang formations. The outcrops of potential saline aquifers and CO_2-EOR reservoirs were studied. Both CMI and its Chinese partners are enthusiastic about sharing their expertise and experience in characterizing the CCUS attributes of the most promising CO_2 storage sites in Wyoming and Shaanxi.
- A field trip to Wyoming Green River Basins (November 2013), which were well-received by the Chinese CERC-ACTC team members, produced highly productive discussions about the CCUS experience and share the design of cooperative projects in both Wyoming and Shaanxi. After the field trip, three research scientists from the NWU continued to work in Laramie at CMI on the following assignments: 1) assemble information regarding the regional geology, structural/stratigraphic framework, and thermal/burial history of the Ordos Basin, and assess the availability of public-domain data; 2) inventory the distribution of energy resources in the Ordos Basin, including oil, gas, and coal; and 3) delineate potential CO_2 sources in the Ordos Basin. Accomplishing these three tasks significantly increased the understanding of CCUS for both countries.
- A field trip (February 2015) to the Huaneng CCUS demonstration project in Bohai Bay and Yanchang Integrated Coal/Petroleum Chemical Industry Park in the Ordos Basin to investigate the opportunities of integrated CO_2 storage with CO_2-EOR and EWR.

Acknowledgements

The University of Wyoming CERC-ACTC project is funded by the U.S. Department of Energy (DE-PI0000017). We acknowledge colleagues who have worked with us on the geological CO_2 storage site characterizations and feasibility study of CO_2-EOR projects in both Wyoming basins and the Ordos Basin in China. We especially acknowledge the assistances of field trip, data analyses and interpretations by our Chinese partners Zhou Lifa, Lifa, Luo Tingting, Chen Yongzhen, Wang Yajun, Bai Yong, and Wang Suli from Shaanxi Provincial Institute of Energy Resources and Chemical Engineering, Gao Ruimin, Jiang Shaojing, Zhao Yongpan, Wang Hong and Huang Chunxia from Yanchang Petroleum Group, Li Xiaochun and Wei Ning from Rock and Soil Mechanic Institute of Chinese Academy of Scinences, and Xu Sisheng and Wang Jinyi from Huaneng Clean Energy Research Institute. Kim Shannon supported this study with outstanding graphical and editorial assistance.

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Simulation and Modeling

Joint Project

U.S. Research Team Lead

- Los Alamos National Laboratory

U.S. Research Team and Industry Partners

- Indiana Geological Survey
- University of Wyoming
- Lawrence Livermore National Laboratory
- Duke Energy

China Research Team Lead

- Chinese Academy of Sciences

China Research Team and Industry Partners

- Shaanxi Provincial Institute
- China Huaneng Group
- Yanchang Petroleum
- Shenhua Group through Chinese Academy of Sciences

Overview

In this thrust area, researchers combined data on capture, policy, economics, and geological utilization and storage to build novel tools to optimize regional carbon capture, utilization, and storage (CCUS) systems. This work focused on high priority CCUS regions in both the U.S. and China, including a report to Huaneng on enhanced water recovery at GreenGen [Los Alamos National Laboratory (LANL), West Virginia University (WVU), Huaneng, Lawrence Livermore National Laboratory (LLNL)], analysis of deep saline reservoirs in the Ordos Basin [University of Wyoming (UWY), Indiana Geological Survey (IGS), LLNL, LANL, Chinese Academy of Science (CAS), WVU, Yanchang Petroleum, Shanxii Provincial Institute], regional scale simulations in Wyoming, Illinois, and the southern U.S. (LANL, IGS, UWY, Duke Energy), the Shenhua CO_2 Pilot Inject Test (CAS, UWY, LANL, Shenhua), and simulation of enhanced oil recovery (EOR) and other novel utilization schemes tied to two regional system analyses tied to Duke Energy's Gibson and Edwardsport facilities (IGS, LANL, UWY, Duke Energy). A major deliverable from this thrust was the release of SimCCS, software that combines diverse aspects of CCUS to allow intelligent business decisions under a range of uncertainty.

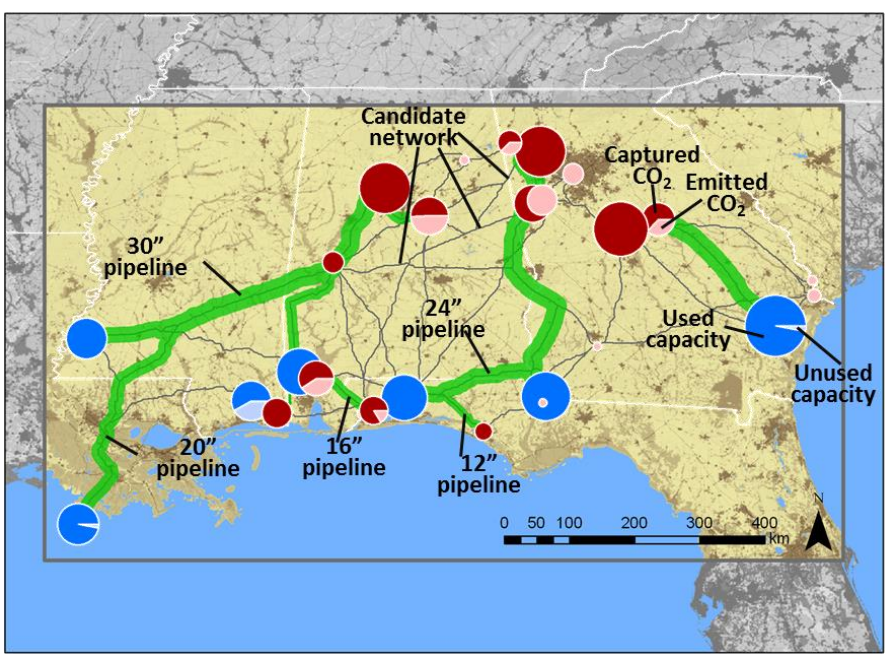

Figure 35: Optimization of CCS infrastructure solution for capturing, transporting, and storing 110 $MtCO_2$ per year for 30 years in the southern U.S. Sources are shown in red and sinks in blue. Pipelines are shown in green with thickness proportional to pipeline diameter.

Research Objectives

Theme 6 in the CERC-ACTC evolved out of a yearlong process of integrating U.S. and Chinese work plans. Through several international meetings and regular working group discussions, detailed plans from both sides were combined into a single Joint Work Plan.

Theme 6.4 employs several types of simulation and modeling work including large 3-D reservoir simulations and system level performance/risk calculations. This task relied heavily on input from Theme 6.1 (Saline Formations at the Basin Scale). As the collaboration grew, the team became focused on two primary risk calculations:

i) subsurface risks for individual injection sites and

ii) risks associated with regional systems of multiple sources of CO_2 connected to multiple subsurface sinks.

Because of strong interest on both the Chinese and U.S. sides of the project, economic concerns were included in both risk components. Target sites for analysis of subsurface risk were chosen in each country including

a) Rock Springs Uplift (RSU) in Wyoming,

b) Ordos Basin in China, and

c) Illinois Basin in the US, tied to Duke Energy's Gibson and Edwardsport facilities.

As the project evolved and new research opportunities arose, we added scope to include: enhanced water recovery (EWR) tied to the GreenGen IGCC power plant in Tianjin China (Subtask 6.6); analysis of the Shenhua Pilot CO_2 injection site in the Ordos Basin, calculations coupling variable electrical grid loading to a CCUS system, the use of high value chemical streams to jump start CCUS, and combining both utilization and deeper saline storage in a single stacked system analysis.

Summary of Research Activities

SUMMARY OF TASKS

During the course of CERC Phase I, several projects grew out of collaborations. These projects are all related, and in some cases highly linked, but have been broken out into five primary groups below.

Ordos Basin Characterization and Simulation (UWY, IGS, LLNL, LANL, CAS, WVU, Yanchang, Shanxii Provincial Institute)

This activity was the first to be tackled and included the entire Theme 6 team. We began by bringing together data on deep saline formations in the Ordos Basin from the Chinese Academy of Science (CAS) and the Shanxii Provincial Institute. Workshops were held to discuss how the data could be merged into a single database. U.S. researchers used U.S. Department of Energy (DOE) products such as the Carbon Atlas to demonstrate how data merging could be done. Part of this analysis was an effort by the Chinese side to gather a comprehensive list of CO_2 sources within the Ordos Basin (Figure 2). These two data sets were combined to create a first of its kind techno-economic analysis for linking sources of CO_2 to deep saline reservoirs in China. This work highlighted large data gaps in available Ordos data relative to more complete US data sets such as those for the Illinois basin. A major outcome of this work were personnel exchanges and collaborative joint research (LANL, CAS, WVU, IGS 2014).

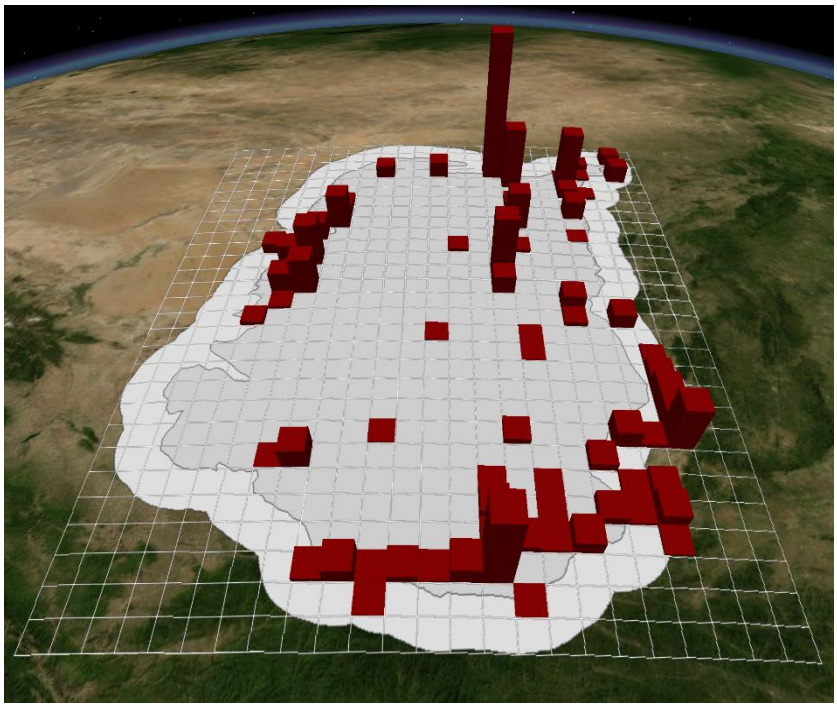

Figure 36: CO_2 Sources in the Ordos Basin

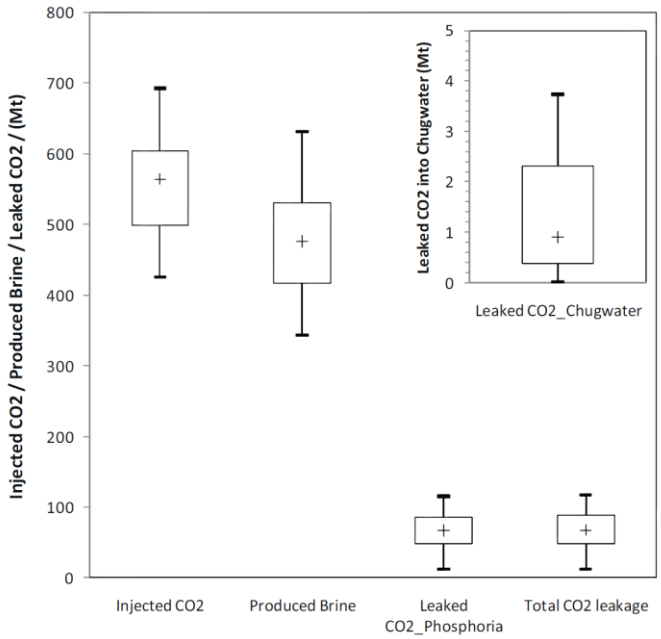

Figure 37: Uncertainties for injected CO2, produced brine, CO2 leaked into the Phosphoria and Chugwater formations, and total CO2 leakage.

Stacked regional system analyses (IGS, LANL, UWY, DUKE)

This activity represents the largest and most complex undertaken in Theme 6.4. Initial work in this area was done to develop statistical methods for exploring uncertainty in storage capacity, injectivity, and leakage for an industrial scale (750 MT in 50 yrs) CO_2 injection site (Rock Springs Uplift, Wyoming, (Figure 3)).

Next we focused on the Illinois Basin in the region surrounding Duke Energy's Gibson and Edwardsport facilities. In this region, we created new high resolution hydrogeological models for the southern Illinois basin. These results formed a template to demonstrate state-of-the-art methods with applications to the Ordos Basin. Further, the new flow models were used to target potential saline storage formations proximal to the Duke Energy Edwardsport/Gibson facilities. (Delivered to Duke Energy LANL, IGS, WVU 2014). Next, we developed a new hierarchical approach to CO_2 storage resource estimation that improves upon the published DOE methodology by providing more robust assessment of resource uncertainty. Initial studies of deep saline formations in the Illinois and Ordos Basins were extended to include all classes of geologic sequestration reservoirs (conventional oil and gas reservoirs, unmineable coals, and organic-rich shales), suggesting that the conventional methodology for CO_2 resource assessment needs improvement with respect to bias and the quantification of uncertainty. As part of this task, we released copyrighted software, SimCCS V.7, a tool that allows users to optimize regional scale systems of capture, injection, and storage. (2015 LANL). The next step was to combined reservoir simulations of shallow conventional utilization targets (EOR) with deeper saline formation simulations to create the first ever analysis of stacked CCUS systems in the region surrounding the Duke Energy Edwardsport/Gibson facilities. (Delivered to Duke Energy in 2015, LANL, IGS). The team then added functionality to LANL's SimCCS system model framework that extends the tool for facilitating business model planning and decision making for potential CCUS technology deployment. This critical development supports decision making that hinges on the potential economic returns derived from CO_2 utilization and storage in both conventional and unconventional reservoir systems (i.e., the first steps in converting SimCCS to SimCCUS). Finally, in late 2015 we assessed prospective resource estimates for enhanced hydrocarbon recovery and CO2 storage in oil and gas (O&G) reservoirs and unconventional hydrocarbons (shale and coal seams) based on comparison to local-scale reservoir model simulations at numerous sites across the Illinois Basin (Figure 4). Results are intriguing as they point to a potential bias in the team's current regional-scale assessments based

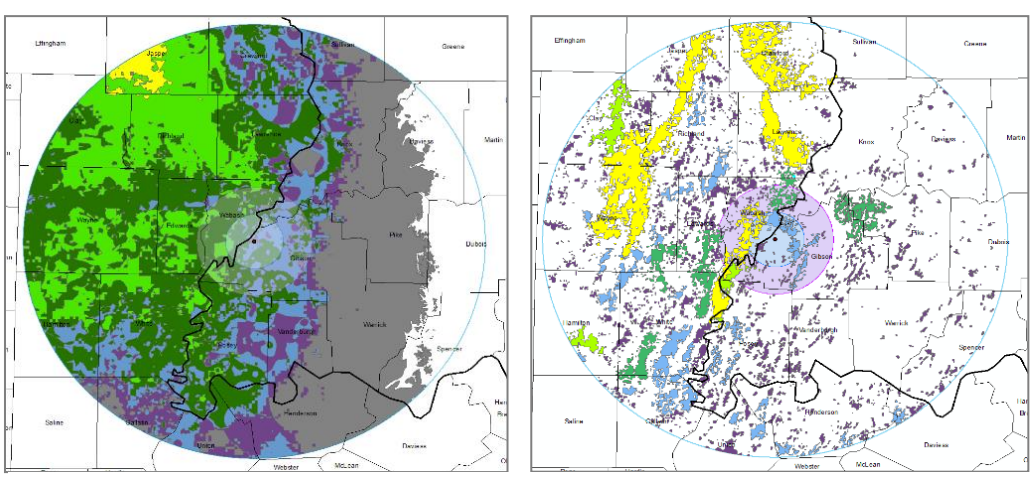

Figure 38: Enhanced coal bed methane recovery (ECBM) and EOR resource evaluation for the southern Illinois Basin.

on the Regional Carbon Sequestration Partnerships (RCSP) methods as reported with updates in the DOE Carbon Atlas. (IGS 2015).

Enhanced Water Recovery (EWR) at GreenGen (LANL, WVU, Huaneng, LLNL)

The strong connections formed in Theme 6 allowed the team to respond quickly to a request by Huaneng Energy to perform calculations of Enhanced Water Recovery (EWR) at the GreenGen IGCC CO_2 capture project in Tianjin China. The team's simulations formed an integral part of a report to the project, highlighting how a new method for managing water withdrawal could be used to reduce risk while generating a source of water. The work underscored differences in regulations of groundwater between the U.S. and China and how such regulations can lead to significant differences in costs between the two countries. This project relied on data exchange from China to the U.S. that was made possible by the CERC program. (2014-2015, WVU, LLNL, U. Wyoming).

Shenhua CO_2 Pilot Inject Test (CAS, UWY, LANL, Shenhua)

We partnered with the CAS to gain access to Shenhua data for a pilot injection site in the Ordos Basin. This project started in the summer of 2015. Access to these data were only made possibly by the trust built over the 4+ years of the project. We sent a Ph.D. student who is an expert user of Petrel and Eclipse (Schlumberger software) to assist CAS in building a numerical representation of the injection tests for three months in Fall 2015.

Other System Analyses

This category includes smaller analyses that developed through discussions with the larger CERC teams and leadership. First, we delivered an analysis of the impacts of variable electricity load generation on CCUS, showing that cost optimized systems do not maximize captured CO_2. These results are published and have received 36 citations demonstrating the usefulness to the CCUS community (Figure 5). We also studied the benefits of using high value chemical streams to jumpstart CCUS. Finally, we described 'Carbon Deserts' in a paper that highlights the mismatch between CO_2 generation, pipeline locations, and utilization (EOR) targets.

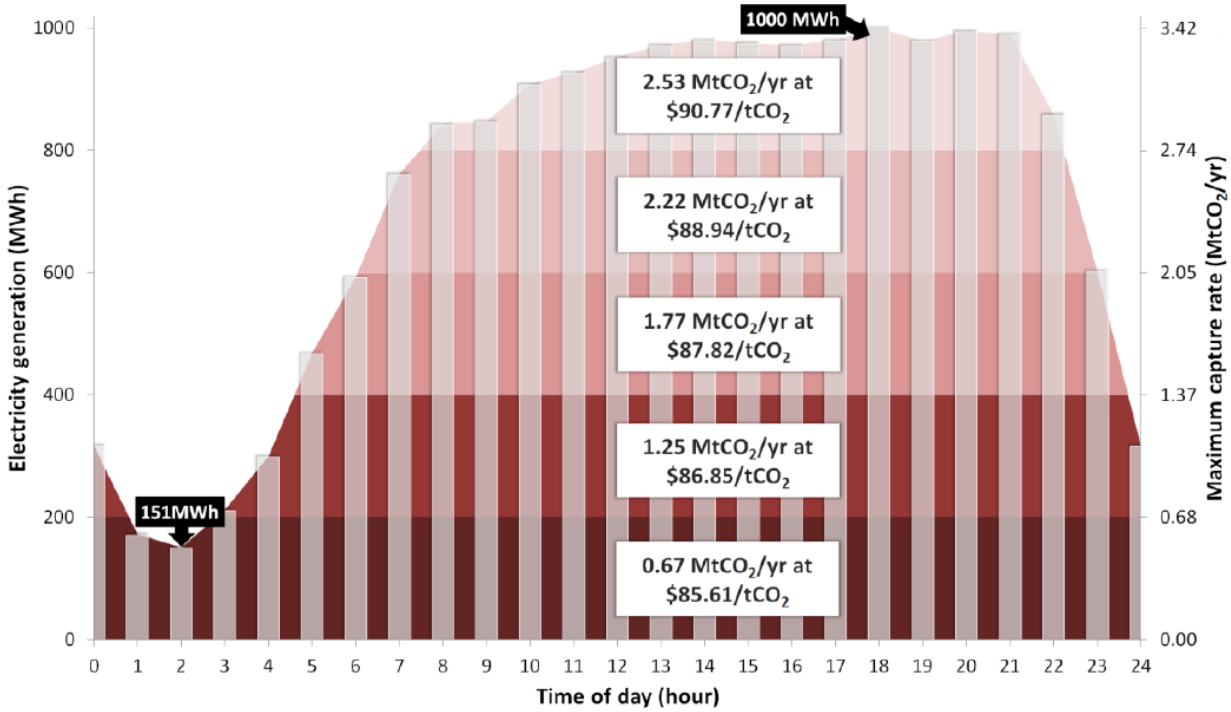

Figure 39: Electricity generation (white columns, primary y-axis) and *capturable* CO_2 (solid areas, secondary y-axis) over a 24 hour period for the average (median) natural gas power plant peaking at 1,000 MWh. The five solid red areas represent the amount of CO_2 that can be captured by installing retrofit equipment on 200, 400, 600, 800, and 1000 MWe of generation capacity. Text in the boxes indicates the exact amount of CO_2 captured and CO_2 management cost for the five capture levels.

MAJOR FINDINGS AND OUTCOMES

Methods that the team has created for estimating storage capacity, CO_2 injectivity, and the linking of multiple CO_2 sources to subsurface sinks will allow projects to more accurately calculate these important metrics. The wider CCUS community has acknowledged the quality and usefulness of the team's work through nearly 150 citations in only 5 years. The team's

methods have been codified in a released software, SimCCS V.7. By showing the business community that coupled utilization (including EOR, ECBM, and enhanced water recovery) and storage can off-set capture costs, the team's tools will allow more projects to move forward in the coming years.

Major Achievements

Copyrighted Software

- 2015 Copyright Disclosure: CODE-2015-183, SimCCS Version 7.0; SimCCS Version 7.0; Primary Author: Richard Middleton; LACC #: LA-CC-15-072.

Figure 40: *SimCCS* software logo.

Workshops

- CERC planning workshop, March 4-6, 2011, Beijing, China.
- Workshop for ACTC-CERC Simulation and Modeling, June 3, 2012, Xi'an, China.
- Working group meeting System integration, simulation and evaluation, February 29-March 1, 2012, Wuhan, China.
- Working group meeting Theme 6, January 8, 2013, Oakland CA.
- Working group meeting Theme 6, October 2, 2013, Jackson Hole WY.
- Workshop on geological modeling its potential applications in Ordos basin and Illinois basin, May 4-9, 2014, Wuhan, China.
- Working group meeting Theme 6, September 19-20, 2014, Hangzhou, China.
- Workshop on use of SimCCS. September 10-14, CAS, Wuhan China.
- Workshop on use of FEHM. September 10-14, CAS, Wuhan China.
- Personnel Exchange, UWY student to CAS for the Shenhua Project., Sept – Dec. 2015, Wuhan China.
- Working meeting with Xioachun Li, September 2015, Los Alamos NM.
- Working group meeting Theme 6, October 4, 2015, Jackson Hole, WY.

List of Publications

- Ziemkiewicz, P., P.H. Stauffer, J. Sullivan-Graham, S.P. Chu, W.L. Bourcier, T.A. Buscheck, T. Carr, J. Donovan, Z. Jiao, L. Lin, J. Wagoner, 2016, Opportunities for Increasing CO_2 Storage in Deep, Saline Formations by Active Reservoir Management and Treatment of Produced Brine: Case study at the GreenGen IGCC Facility, Tianjin, PR China. Accepted pending revisions, Int. J. Greenhouse Gas Control.
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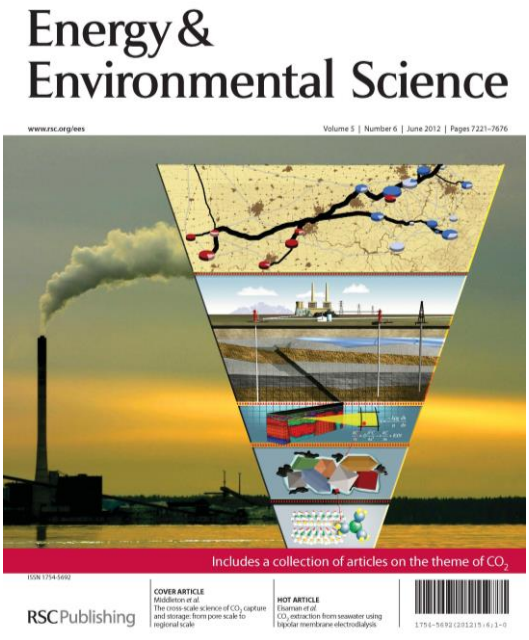


Figure 41: Journal Cover tied to CERC work.

Additional Funding

- LANL, UWY, and LLNL partnered to submit a proposal based on our characterization, simulation, and risk analysis results from CERC. The title of the funded project is "Field Demonstration of Reservoir Pressure Management through Fluid Injection and Displaced Fluid Extraction at the Rock Springs Uplift, a Priority Geologic CO_2 Storage Site for Wyoming" PROJECT AWARD: DE-FE0026159

Commercialization

One of the primary successes of Subtask 6.4 is the release of copyrighted software, *SimCCS* V.7, a tool that allows users to optimize regional scale systems of capture, injection, and storage (2015 LANL). The team traveled to CAS in China to present a workshop on how to use this software. The latest developments that will turn *SimCCS* into *SimCCUS* will have great commercial potential because of the business planning and decision making components.

Collaboration

The team initially proposed a techno-economic analysis of the southern Illinois Basin in January, 2012. Industry partner Duke Energy was helpful in refining team research goals and directions. The team was able to produce two reports that should be useful to the company if they decide to pursue EOR or other hydrocarbon utilization by capturing CO_2 from their fleet of power plants.

The team began CERC collaboration by meeting with the Chinese Academy of Sciences, Yanchang Petroleum, and Shaanxi Provincial Institute while working on Research Activity 3a above. The relationships built, especially with CAS, resulted in personnel exchanges between CAS and LANL. Through these exchanges the team was able to publish joint research. Later, these CERC relationships resulted in expansion of scope to include GreenGen EWR and Shenhua Pilot CO_2 Injection projects.

Conclusions

Based on this body of work, the team has concluded that detailed, data intensive analyses are needed to allow robust and intelligent business decisions for development of regional scale CCUS projects that involve multiple sources of CO_2 linked to multiple potential reservoirs. The size and complexity of such projects require intricate coupling of physics, chemistry, economics, and policy, a task that is only achieved through advanced simulation tools driven by high resolution, site specific data.

International Standards on CCS TR 27918-Lifecycle Risk Management for Integrated CCS Projects

Joint Project

U.S. Research Team Lead

- **World Resources Institute**

China Research Team Lead

- **Chinese Academy of Sciences-Institute of Rock and Soil Mechanics**

Overview

In this research area, World Resources Institute (WRI) is engaged as a liaison to the development of international standards for carbon capture and sequestration (CCS) (ISO TC265). Sarah Forbes, former staff at WRI, and Yang Xiaoliang have both been appointed to Working Group 5 (WG5), Cross Cutting Risks Issues. The ISO TC 265 is chaired by Canada with China as the mirror chair. The technical report (TR27918) addressing the overall risks associated with CCS projects has been co-developed by Chinese Academy of Sciences- Institute of Rock and Soil Mechanics and WRI.

Research Objectives

This study informs future development of a standard for overall risk management for CCS projects. The scope includes lifecycle risk management issues for integrated CCS projects. The specific risks associated with any one stage of the CCS process (capture, transportation, or storage) are covered by the respective section of the Standard. Therefore the focus is limited to risks that affect the overarching CCS project or risks that cut across capture, transportation, and storage.

Summary of Research Activities

SUMMARY OF TASKS

- Literature review on relevant guidelines, standards, and regulations on risk management on CCS projects
- Experts interview to identify risks, the obtain risk evaluation and rating methodologies, and to learn risk management plans, etc.
- Coordinate international experts in this field to draft an international standard technical report (TR 27918) regarding risk issues for integrated CCS projects

MAJOR FINDINGS AND OUTCOMES

The team has completed two drafts of Technical Report 27918, and discussed the TR in two annual meetings in 09/2015, 05/2016. The team has developed a draft-version guidelines regarding on life-cycle risks management on integrated CCS projects.

Major Achievements

Standards, Codes and Policies influenced

- Technical Report that has been influencing Chinese National Standards development on CCS projects.

Workshops

- ISO/TC 265 Carbon dioxide capture, transportation, and geological storage 2015 Annual Work Meeting in Oslo, Norway 09/2015

List of Publications

- TR27918 CCS — Lifecycle risk management for integrated CCS projects

Collaboration

WRI has been working closely with Chinese Academy of Sciences-Institute of Rock and Soil Mechanics to develop the guidelines/methodologies for life cycle risks management of large-scale CCS projects. Since this is still an emerging issue in the both countries and the rest of the world, working with our Chinese partners will not only help ensure the safety and environmental sustainability of CCS projects, but also shape how the rest of the world on life cycle risks management on CCS.

Conclusions

The significant opportunity for developing life cycle risks for integrated CCS projects is truly bringing the best research organizations in the U.S. and China together. This work ultimately improves global practice of how to safely and effectively design/operate CCS projects.

Figure 42: ISO TC265 WG5 Group Meeting in Oslo, Norway, September 2015 & Xiaochun of CAS-WHRSM and Sarah Forbes of DOE (formerly with WRI) are co-leading discussions on TR27918.

Pre-feasibility Study for Active Aquifer Management

Joint Project

U.S. Research Team Lead

- **West Virginia University**

U.S. Partners

- **Lawrence Livermore National Laboratory**
- **Los Alamos National Laboratory**
- **University of Wyoming**

China Partners

- **Huaneng**

Overview

Capture and storage of CO_2 from fossil fuel burning is a key element in the global imperative to control greenhouse gases. Carbon capture, utilization and storage (CCUS) seeks beneficial applications for recovered CO_2. This project studied enhanced water recovery (EWR) as the primary application. Secure carbon storage requires identification of suitable geological formations that will have the capacity to store large volumes of CO_2 while preventing its escape to the atmosphere. Suitable storage formations will have inter-connected voids (spaces between rock grains) to allow the injected CO_2 to permeate the formation. In addition, suitable storage formations will be covered with impermeable rock to permanently trap the CO_2 underground. These rock formations are found at considerable depth-thousands of meters below the surface where their void spaces are normally filled with saline water. This pre-feasibility study evaluated the potential for removing this water to create additional storage capacity for CO_2 while treating the extracted water so that it can be used for industrial use. Known as active reservoir management, the process would also better constrain CO_2 movement within the target formation.

This project is studying the GreenGen site in Tianjin, China where Huaneng Corporation is capturing CO_2 at a coal fired IGCC power plant. Known as the Tianjin Enhanced Water Recovery (EWR) project, the rock units in the vicinity of the plant were evaluated for CO_2 storage potential. Treatment options were then developed for the brine that would be produced. This pre-feasibility study was conducted to determine whether a detailed engineering effort is warranted. In addition, the project is intended to develop protocols for identifying suitable sites for CCUS/EWR.

This project is intended to assist Huaneng in its development of a carbon storage strategy for GreenGen. Evaluation of storage options will require appropriate reservoir conditions and the assurance that CO_2 storage volumes and injection rates meet expectations. Several fundamental assumptions are involved:

- Reservoir capacity
- Adequate hydraulic conductivity throughout the reservoir
- CO_2, formation brines and reject brines will not form scale/precipitates and interfere with reservoir conductivity
- Withdrawal of formation brines will increase effective CO_2 storage capacity
- The selected brine treatment strategy will meet technical and financial expectations

Failure to meet any of these assumptions may have serious financial implications for the GreenGen project and require major additional investment/corrective measures after the project has gone on line. The value of this project is to provide the company with a comprehensive evaluation of the reservoir management and brine treatment options to lessen uncertainty prior to finalizing project designs.

The EWR project was led by West Virginia University (WVU) in partnership with Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL) and the University of Wyoming (UWY). The U.S. team worked with Chinese CERC collaborators to identify geological conditions, plant requirements and costs.

Active Reservoir Management

While many important parameters remain to be studied, a strong body of literature by Chinese scientists has provided the basis for assessing the feasibility of proceeding with a detailed study to develop a plan for CCUS/EWR for the GreenGen facility.

Injection of CO_2 into the subsurface creates high pressure regions around injection wells. Storage capacity is partly controlled by pressure buildup in the area around the injection wells. Pressure build-up is generally not permitted to rise above hydrofracture pressure to ensure the integrity of the sealing rocks. Pressure build-up is a function of injection rate, fluid properties, rock porosity, rock permeability to both water and CO_2, and the connectivity of permeability at the kilometer scale.

There are two options for management of pressures within the target reservoir: passive and active. Under passive management, CO_2 displaces formation water (brine) and the resulting plume moves in response to uncontrolled pressure gradients in the reservoir rock. In active management, brine is withdrawn (produced). Brine production serves two primary purposes. First, brine production provides pressure relief and allows CO_2 to flow toward the lower pressures regions. Second, brine production opens pore volume for CO_2 migration, thus increasing the storage capacity of the reservoir. Active management can also be used to create preferential zones for CO_2 migration and can help to control the CO_2 distribution throughout the reservoir.

In active management, produced brines are brought to the surface and treated to supplement agricultural, human use, or industrial process water. Significant volumes of treated water may be made available. For example, Huaneng's GreenGen power project captures 100,000 t CO_2/year which could displace 125,000 m^3 of formation water (238 L/min). Treatment of brines to industrial, agricultural, or human use standards is well understood, though the optimal treatment train for a specific brine and its associated cost should be based on the logistics and chemistry of a specific saline aquifer. Another important factor in the system level cost calculations is to include the use and disposal of treatment byproducts (e.g., salt cakes, brine concentrates, thermal energy, and mineral resources). Members of our team have done preliminary work on the cost/benefit analysis for low temperature geothermal energy extraction coupled with aqueous phase Lithium mining and CO_2 injection.

Research Objectives

Evaluation of this opportunity will involve a two phase project. The pre-feasibility study is meant to determine whether the concept has merit and adds value to Huaneng and to CERC-ACTC. Specifically, it aims to gain a better understanding of the following:

- The technical feasibility of the EWR concept
- The suitability of the reservoir properties
- The reservoir storage (caprock) integrity
- Development of a legitimate Injection/withdrawal strategy?
- Cost estimates for water treatment and reservoir management

Overall, this project will evaluate the feasibility of withdrawing water in order to increase storage reservoir capacity, decrease leakage risks, and provide a water source through desalination of produced water. Additional benefit may be gained by extraction of mineral resources (e.g., lithium) from the produced water. Specific objectives include:

- Development of an active reservoir management scheme including production of deep saline water that will
  - Optimize storage of the CO_2 generated by the Tianjin IGCC unit
  - Maximize reservoir storage capacity
  - Reduce reservoir overpressure and related leakage risks
  - Combine modeling strengths from LANL and LLNL (Figure 02)
- Identification of treatment strategies to gain useable water from produced brine
- Use of heat from produced water in desalination or mineral extraction processes
- Develop beneficial uses for byproduct brines/salts
- Combine the results into a system analysis that will explore uncertainty (risk) in both physical processes and economic feasibility.

Summary of Research Activities

SUMMARY OF TASKS

Conducted an eight week pre-feasibility study that addressed key unknown factors and made a preliminary analysis of the reservoir management and water treatment opportunities:

1. Worked with Chinese colleagues at Chinese Academy of Sciences (CAS) and published literature to address the following critical unknowns:
   - Brine chemical composition-both produced and treatment reject brines. The latter will be estimated based on produced brine chemistry and treatment method.
     - Build on existing knowledge and data bases from LLNL, WVU, UWY, and LANL for desalination costs built from interaction with industrial contacts.
     - Work with Chinese CERC collaborators to generate costs for systems in China
   - Hydraulic conductivity of the target reservoir rock
     - Leverage existing CERC relationships to gain access to porosity, permeability, and facies data from the GreenGen subsurface (CAS, Yanchang Oil, Northwest University, Tshingua U.).
     - Estimate CO_2 injection rates and formation water withdrawal rates to avoid development of excessive pressure gradients
     - Suggest modeling strategies that use the best of our existing capabilities (LLNL, WVU).
     - Use coupled economic/technical models to simultaneously optimize well spacing, pumping rates, storage capacity, and extracted resources.
   - Chemical interactions between injected CO_2, reject brines and formation brines at prevailing pressures/temperatures.
     - Use geochemistry codes (PFLOTRAN/FEHM/NUFT) and knowledge gained from prior simulations and field experiments of CO_2 injection (In Salah, Sleipner, Cranfield) to guide Phase 2 plans.
2. Developed cost/performance model
3. Evaluated reservoir management/brine treatment options
4. Developed a reservoir management strategy
5. Identified a brine treatment, handling strategy
6. Developed strategy for the Phase 2 study
7. Wrote final report.

SITE GEOLOGICAL AND HYDROGEOLOGIC CONDITIONS

The Bohai Bay Basin (BBB) in eastern coastal China was examined for a CO_2 storage resource assessment south of Tianjin in the immediate vicinity of the Huaneng GreenGen IGCC facility in Binhai New Area near Tanggu (Figure 1). The BBB is a Mesozoic–Cenozoic rifted sedimentary basin consisting of a series of fault-bounded sub-basins (sags) filled by thick continental Paleogene (Eocene), clastic sediments (Figures 1, 2). A regional unconformity at the top of the syn-rift sediments separates Paleogene and older sediments from Neogene to recent strata, which were deposited during post-rift thermal subsidence. Major faults form Paleogene half-graben and growth-fault structures and relative uplifts (heaves) that define smaller sub-basins (sags) in the north-central portion of the BBB (Figure 3). Faulting related to post-rift thermal subsidence continues in the Neogene and may reach to the present day surface (Figure 3).

The regional stratigraphy, from the top to the bottom, consists of basin-wide continental sandstone and clay Quaternary sediments (250–550m thick) (Figures 2, 3), which are underlain by the Neogene continental post-rift interbedded sandstone and mudstone beds of the Minghuazhen Formation (230-1300m thick) (Figures 2, 3). The numerous interbedded mudstone units of the Minghuazhen (Nm) stretch across the entire basin and are assumed to form multiple regional seals (Yang et al. 2013). The lower portion of the Minghuazhen is dominated by mudstone, inter-layered with fine-grained sandstone, and is considered the primary regional seal for containment. The underlying post-rift Neogene Guantao Formation (Ng) is widely distributed across the basin but thins and can be absent on structural highs (0–1520m thick) (Figures 2, 3). The Guantao consists of sandstone inter-layered with poorly sorted pebbly sandstone inter-layered with mudstone toward the base. The Guantao is characterized by relatively low salinity water and high porosity and permeability. The Neogene is separated by a regional unconformity from the Paleogene syn-rift units. The uppermost unit, the Eocene Dongying Formation (Ed) (0-400m) (Figure 2, 3) is a heterogeneous unit consisting of sandstone,

mudstone, oil shale and limestone that thickens near bounding faults of sags. Salinity increases in the Dongying Formation but remains relatively low. Porosity and permeability in the sandstone units of the Dongying can be very good especially along faults bounding sags. These form numerous hydrocarbon reservoirs characteristic of the BBB.

Guantao CO_2 Storage Reservoir Properties

The base of the Neogene Guantao Formation, a target CO_2 storage horizon, is composed of sandstone, sandy gravel, and gravel. The sandstone units consist of quartz, feldspar (including albite and anorthite), montmorillonite, illite, kaolinite, and minor chlorite (Pang et al., 2012). Based on reported data, the permeability of sandstone in the Guantao Formation varies from 800–2000 mD, while the porosity is 18–38% (Hu, 2002; Pang et al. 2012, Yang et al., 2013). Core analyses from a single well from the Qikou sag to the south of Tanggu (Figure 1) shows the excellent porosity and the range of permeability in the Guantao Formation (Table 1).

Water samples from the Guantao and related Neogene formations have reported salinities of 800–1000 mg/L, and are of HCO_3-Cl–Na or Cl-HCO_3–Na types (Pang et al. 2012; Yang et al. 2013; Table 1). Water pH determined in situ indicates that the water is neutral to alkaline with an average pH of 7.7 (Pang et al., 2012). Pressure gradient appears to be hydrostatic.

Dongying CO_2 Storage Reservoir Properties

Beneath the regional unconformity, the Dongying Formation was deposited during the waning stage of rifting and shows a coursing upward trend from fine grained rocks mainly lacustrine mudstones and oil shale at the base to deltaic sandstone at the top. The uppermost sandstone units interbedded with this mudstone beds of the Dongying Formation are another target for CO_2 storage. Based on reported data, the permeability of sandstone in the Dongying varies from 200–1000 mD, while the porosity is 20–32% (Yu, 2010, Lin et al., 2010; Pang et al. 2012, Yang et al., 2013). Core analyses from a single well from the Qikou sag to the south of Tanggu shows the good porosity and the range of permeability in the Dongying Formation (Figure 4, Table 3).

Water samples from the Dongying have reported salinities of around 3,000 mg/L, and are of HCO_3-Cl–Na type (Meng, 2007) (Table 4). Water pH determined in situ indicates that the water is alkaline with an average pH of 8.29 (Meng, 2007). Downward from the top of the Dongying Formation, salinity and pressure increase rapidly with depth, and the unit is significantly over-pressured (Figure 5).

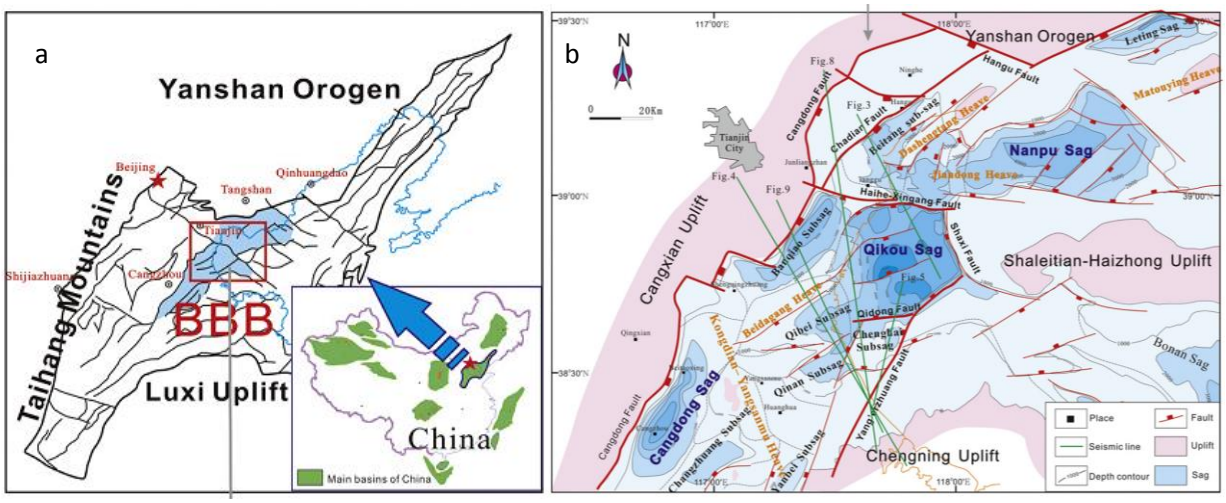


Figure 1: a) Location and structural framework of the BBB in eastern coastal China with highlighted study area south-east of Tianjin. b) Structural framework of the study area in the immediate vicinity of the Huaneng GreenGen IGCC facility in Binhai New Area near Tanggu. Modified from Zhou et al., 2012.

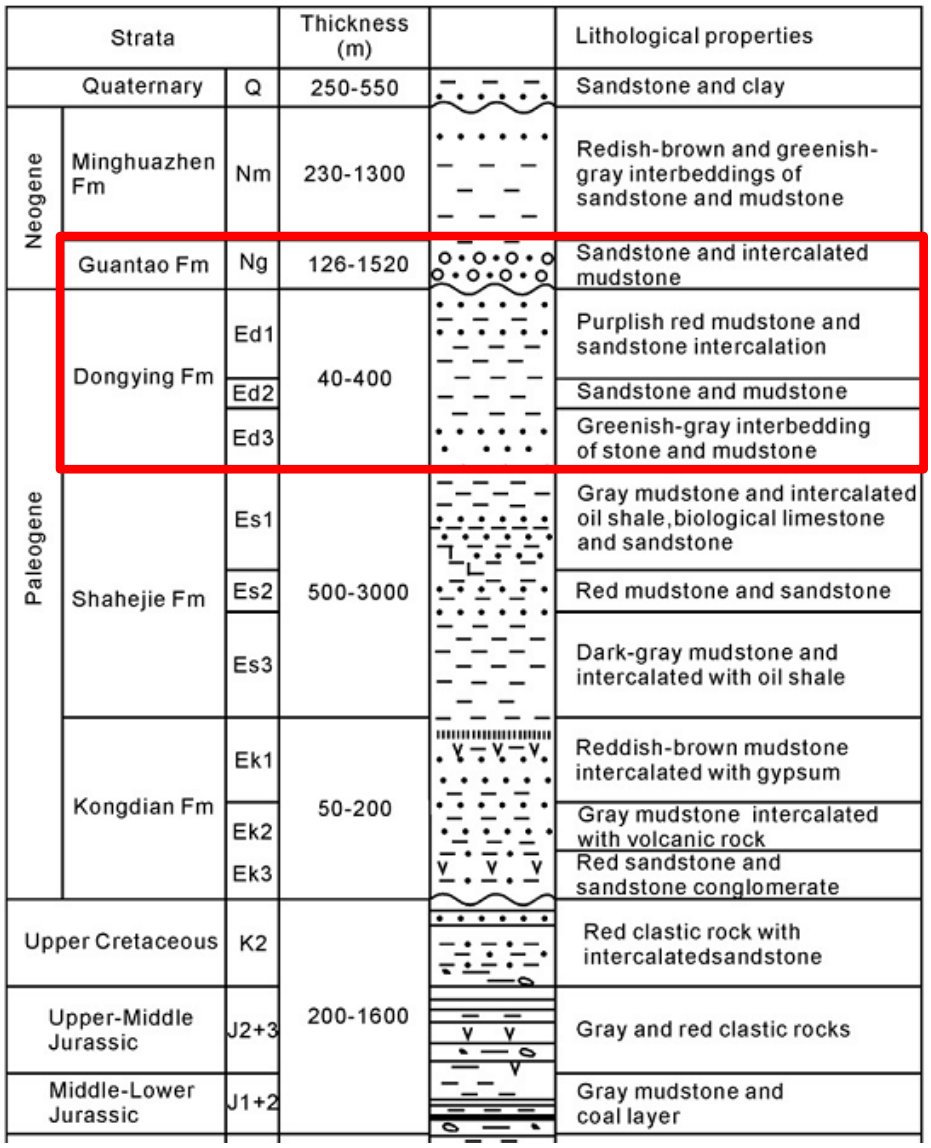


Figure 2: Stratigraphy of north-central BBB modified from Yang et al. 2013. The Guantao and Dongying formations, target CO_2 storage reservoirs for the assessment are highlighted.

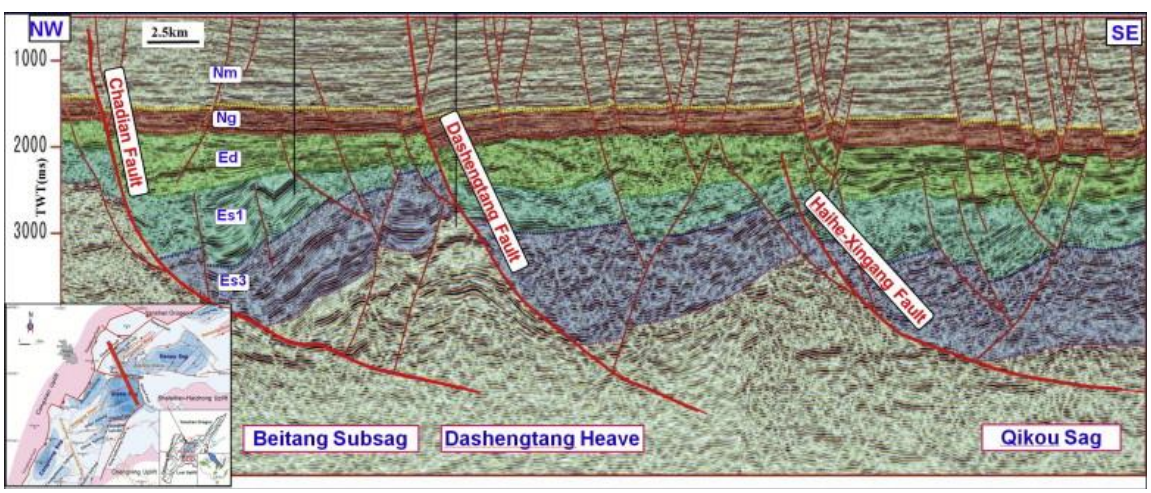


Figure 3: Seismic profile through the Tanggu area of the northern BBB showing major faulting defining Paleogene half-graben and growth-fault structures that define relative uplifts (heaves) separating smaller sub-basins (sags). Faulting related to thermal subsidence continued in the Neogene. The target units for CO_2 storage resource assessment are the Neogene Guantao Formation (Ng), and Eocene Dongying Formation (Ed). The Neogene Minghuazhen Formation (Nm) is interpreted as a regional seal for CO_2 containment. Figure from Zhou et al., 2012.

Table 1: Core analyses from the B16 well in the Qikou Sag south of Tanggu as reported by Yang, 2010.

Depth	ϕ (%)	K (mD)
1383.06	28.34	21.6
1384.54	34.4	184.6
1385.46	29.91	183
1387.14	36.7	1064.1
1387.73	30.7	21.1
1393.13	30.1	12.1
1395.15	31.6	7.8
1396.86	34.7	6873.7
1400.54	34.3	208.3
1401.93	36.4	3473
1403.69	33.04	232.3
1406.41	34.3	387.8
1409.16	36.39	2874.4
1413.43	32.5	39.8
1413.92	36.2	1274.1
1414.55	30.1	53.6
1416.04	35.52	1318.3
1416.56	32.1	113.3
1419.68	34.8	157.6
1420.5	31.15	37.3
1420.89	36.9	1470.7
1437.62	36.65	4886.5

Table 2: Chemical analysis of formation water from the Guantao Formation (Ng) and overlying Minghuazheng Formation (Nm). Concentration of major elements reported in mg/L. From Pang et al., 2012 (Table 2).

Sample ID	Formation	T (°C)	pH_f	F	Cl	NO_3	SO_4	HCO_3	Ca	Mg	Na	K	SiO_2	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{13}C$ (‰)	^{14}C (pmc)	TDS (g/L)
TG08	Nm	40.4	8.2	3.2	52.1	0.1	53.4	596	5.1	0.8	309.0	4.5	22.0	−9.26	−73.0	−13.1		0.75
TG10	Nm	46	8.4	4.3	21.2	0.0	28.2	669	4.6	0.7	293.0	4.1	25.9	−10.00	−72.4	−13.4		0.72
TG13	Nm	43	8.6	4.0	85.1	0.8	73.8	590	10.0	2.0	300.0	11.8	29.8	−9.36	−72.6	−11.6		0.81
DL20	Nm	51	8.2	5.7	300.8	3.3	205.5	513	24.0	7.8	434.0	44.0		−8.82	−73.4			1.28
DL31	Nm	47	8.0	5.4	296.5	1.4	200.9	560	26.0	8.1	439.0	44.0		−8.87	−71.4			1.30
DG49	Ng	58	8.2	7.7	605.4	0.8	181.2	559	18	7.5	579	44		−7.54	−68.0			1.72
DL10	Ng	62	7.2	7.2	316.6	1.3	202.8	610	34.3	6.8	467.0	39.2	29.9	−9.38	−73.3	−6.1	12.79	1.42
DL25	Ng	73	7.0	9.6	336.6	0.0	228.2	530	60.0	17.5	503.0	98.0		−8.30	−73.6			1.52
HX38	Ng	53.5	7.9	3.9	221.5	0.6	320.4	455	45.0	6.9	418.0	44.0		−9.46	−72.2		7.58	1.29
JN02	Ng	64	7.4	8.3	423.3	0.0	240.1	616	47.0	6.7	534.0	70.0		−9.10	−72.1		1.74	1.64
KF01	Ng	60	7.7	5.3	225.5	1.3	163.2	645	11.6	0.9	477.0	10.0	39.8	−9.64	−71.8	−7.4	12.2	1.26
KF02	Ng	66	7.6	6.9	258.0	0.1	175.3	635	10.9	0.9	496.0	9.8	39.7	−9.95	−71.1	−6.8	14.65	1.32
TG03	Ng	72	8.0	5.8	305.8	1.5	191.6	645	12.0	1.0	531.0	11.4	43.4	−9.18	−72.0	−8.9	12	1.43
TG05	Ng	70	7.4	5.7	315.5	1.1	220.5	641	12.7	1.0	546.0	10.1	40.7	−9.21	−72.7	−7.1	10.48	1.47
TG14	Ng	70	7.6	4.9	272.7	2.2	172.0	670	10.8	1.1	519.0	11.5	48.0	−9.45	−72.2	−8.9	11.24	1.38
TG18	Ng	60	7.7	6.4	284.6	1.2	196.9	620	12.9	1.3	491.0	10.4	38.6	−9.08	−71.0	−7.2	14.9	1.35
TG19	Ng	63	7.5	6.7	324.8	1.1	208.6	651	14.0	1.4	557.0	10.9	38.8	−8.90	−72.2	−6.5	9.09	1.49
TG20	Ng	63	7.4	4.5	277.4	1.5	184.7	641	14.7	1.4	509.0	10.5	37.1	−9.16	−72.6	−5.9	10.76	1.36
TG24	Ng	46.4	7.6	5.6	204.9	1.0	143.9	613	23.1	4.8	397.0	32.1	33.5	−9.40	−72.9	−8.0	10.72	1.15
TG38	Ng	66	7.9	6.0	273.3	0.4	205.4	673	14.0	7.0	476.0	45.0		−9.24	−72.2			1.36
TGR28	Ng	64	8.4	6.5	359.8	0.9	240.6	479	11.8	0.8	502.6	3.5	38.0					1.65
TR19	Ng	54	7.7	6.2	258.8	0.0	173.7	611	18.8	3.1	465.0	17.7	33.0	−9.36	−73.3	−6.4	7.1	1.28
TR19B	Ng	36	7.7	6.9	356.7	0.8	233.6	602	19.5	3.2	523.0	18.0	34.9	−9.34	−72.1			1.50
TR20	Ng	36	7.8	5.2	283.4	1.5	182.9	606	19.0	3.1	444.0	18.0	33.3	−9.43	−73.1			1.29

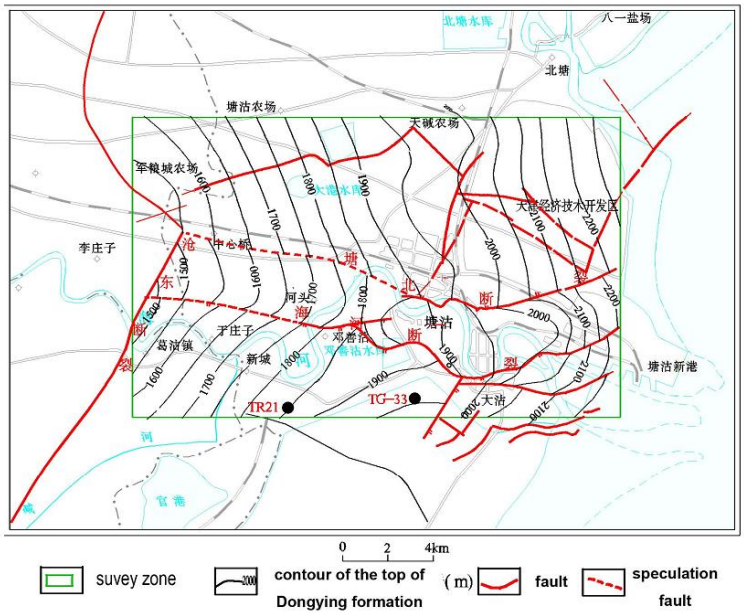


Figure 4: Location of Well TR-21 from the Dongying Formation in relation to Tanggu with porosity and permeability reported in Table 3. From Lin et al., 2010.

Table 3: Reported porosity and permeability from a sandstone units in well TR-21 from the Dongying oil reservoir. Location of well in relation to Tanggu is shown in Figure 4. From Lin et al., 2010.

Formation	Depth(m)	Thickness(m)	Porosity (%)	Permeability(mD)
Ed1	1950.1~1963.1	13	27.51	625.25
	1978~1984	6	26.64	480.03
	1989.4~1996.7	7.3	23.35	218.93
Ed2	2073.3~2090.1	16.8	31.41	908.16
	2202.2~2207.6	5.4	31.02	812.55
Ed3	2213.0~2220.0	7	29.98	725.69
	2249.7~2278.8	6.4	25.94	389.88
	2272.3~2278.8	6.5	26.04	406.29
	2284.3~2312.6	28.3	23.41	275.69
	2320.2~2324.9	4.7	26.41	421.98

Table 4: Chemical analysis of formation water from the Dongying Formation. Concentration of major elements reported in mg/L. Samples from well Tang 20-2 to the south of Tanggu. Reported depth 2199-2454 meters, with a temperature of 85°C and in situ pH of 8.29. From Meng, 2007.

Cation, mg/L		Anion, mg/L		Other index, mg/L	
K^+	9.4	Cl^-	1258.5	Soluble SiO_2	58.4
Na^+	1190	SO_4^{2-}	40.1	Free CO_2	0
Ca^{2+}	8.4	HCO_3^-	872.6	TDS	3438.3
Mg^{2+}	0.9	CO_3^{2-}	0	Total Solids	3002
NH^{4+}	3.1	NO_2^-	<0.002	COD_{Mn}	12.33
Cu^{2+}	<0.02	NO_3^-	10.66	Total Hardness(as $CaCO_3$)	24.5
Mn^{2+}	0.02	F^-	3.5	Permanent Hardness (as $CaCO_3$)	0
Zn^{2+}	0.37	Br^-	5	Temporary Hardness (as $CaCO_3$)	24.5
TFe	0.42	I^-	1.25	Negative Hardness(as $CaCO_3$)	691.1
TCr	0.003	PO_4^{2-}	0.04	Total Alkalinity(as $CaCO_3$)	715.6
Pb^{2+}	<0.01	HBO_2^-	15.29	Total Acidity (as $CaCO_3$)	0
Cd^{2+}	<0.001				

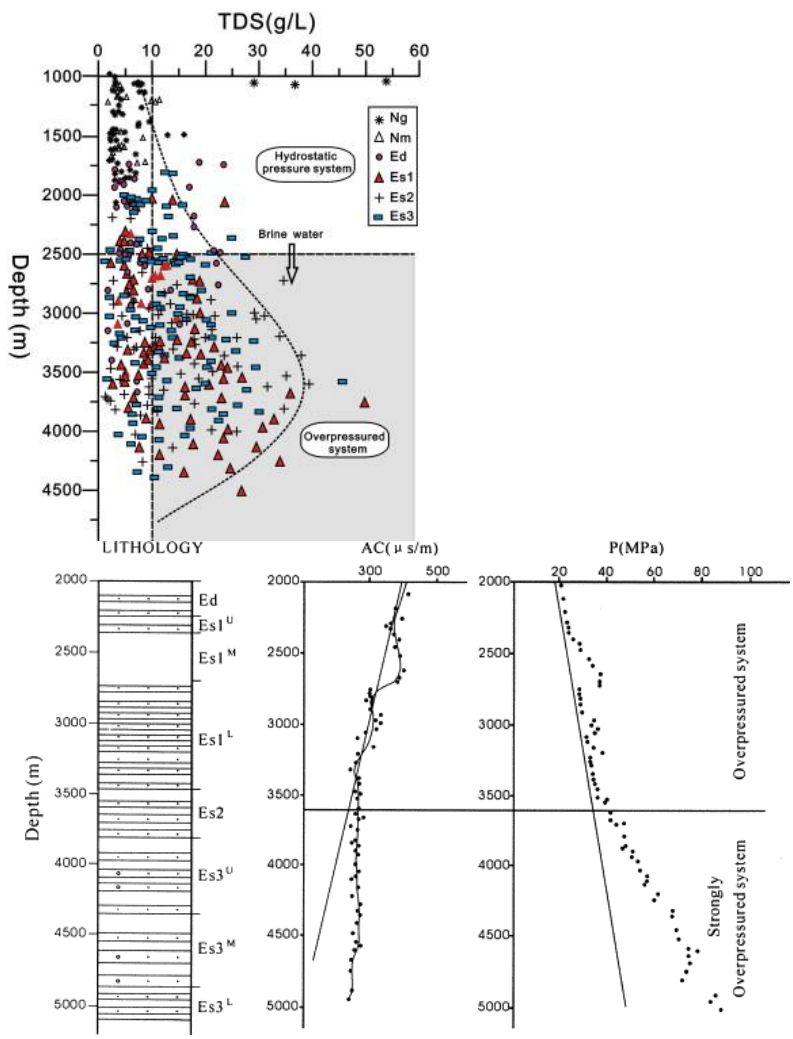


Figure 5: Variation of total dissolved solid (TDS) with depth and pressure in the Neogene and Paleogene formations in the Qikou sag. Pressure and salinity increase rapidly above the top of the Paleogene. From Du et al., 2010.

RESERVOIR PERFORMANCE ANALYSIS

Injection of CO_2 into the subsurface creates high pressure regions around injection wells. Storage capacity is partly controlled by pressure buildup in the area around the injection wells. Pressure build-up is generally not permitted to rise

above hydrofracture pressure to ensure the integrity of the sealing rocks. Pressure build-up is a function of injection rate, fluid properties, rock porosity, rock relative permeability to both water and CO_2, and the connectivity of permeability at the kilometer scale.

Huaneng is operating an IGCC unit near Tianjin (Tanggu, Figure 6a) that is currently capturing about 0.1 MT (millions of tonnes) of CO_2 per year. Future plans call for an increase to between 1-2 MT of captured CO_2 per year. Huaneng's project plans call for injection of captured CO_2 into a deep, saline reservoir for permanent storage. For this study the target injection reservoirs (Neogene Guantao (Ng) and Paleogene Dongying (Es) formations) within the Qikou Sag of the larger BBB are at depths between 1500-2500 m and are saturated with brackish formation water in the range of 700-16000 ppm total dissolved solids. These formations received positive recommendations related to CO_2 storage from Yang et al. (2013). The location of the study area relative to the IGCC plant (GreenGen) is shown in Figure 6b. Using a geologic model of the area, a site was chosen to the west of GreenGen in a fault bounded block approximately 5 km x 15km. Figure 6 shows hypothetical injection and production well locations within this block.

The team presents initial estimates of CO_2 injectivity and plume radius for injection of 0.1 MT/yr and 1 MT/yr. Results for 1 and 10 years of injection are used to show how the plume from a single injector well could grow through time for a simplified, idealized system. Most results are for a 2 km deep injection well, while several results from a deeper plume are also presented to demonstrate the impact of changing depth and temperature.

CO_2-PENS Radius and Injectivity Calculations

The team uses CO_2-PENS (Predicting Engineered Natural Systems), a system analysis tool developed using the GoldSim© platform (GTG 2010). GoldSim© is used to develop analysis models that perform multi-realization, probabilistic simulations. A FORTRAN dynamic link library (DLL) is used to calculate plume radius using the following equations presented in Stauffer et al., 2009.

To calculate the CO_2 plume thickness, b, as a function of radius and time (r and t) the team uses the analytical expression given by Nordbotten et al. (2005):

$$b(r,t) = B\left(\frac{1}{\lambda_c - \lambda_w}\right)\left(\sqrt{\frac{\lambda_c \lambda_w V_t}{\phi \pi B r^2}} - \lambda_w\right) \quad (1)$$

where λ_c and λ_w are the CO_2 and water mobilities (the ratio of phase relative permeability to phase viscosity), and V_t is the total available volume of CO_2. Equation 3 can be solved for the maximum plume radius, r, at a given time by setting the plume thickness, b, to zero as:

$$r = \sqrt{\frac{\lambda_c V_t}{\lambda_w \phi \pi B}} \quad (2)$$

Injectivity is calculated using a reduced order model (complex function) based on thousands of simulations of injection into a 2D radial mesh with varying thickness, depth, temperature, and excess pressure of injection (Middleton et al., 2012). Finally, excess pore pressure (EPP) in the injection interval is calculated based on the specified flow rate.

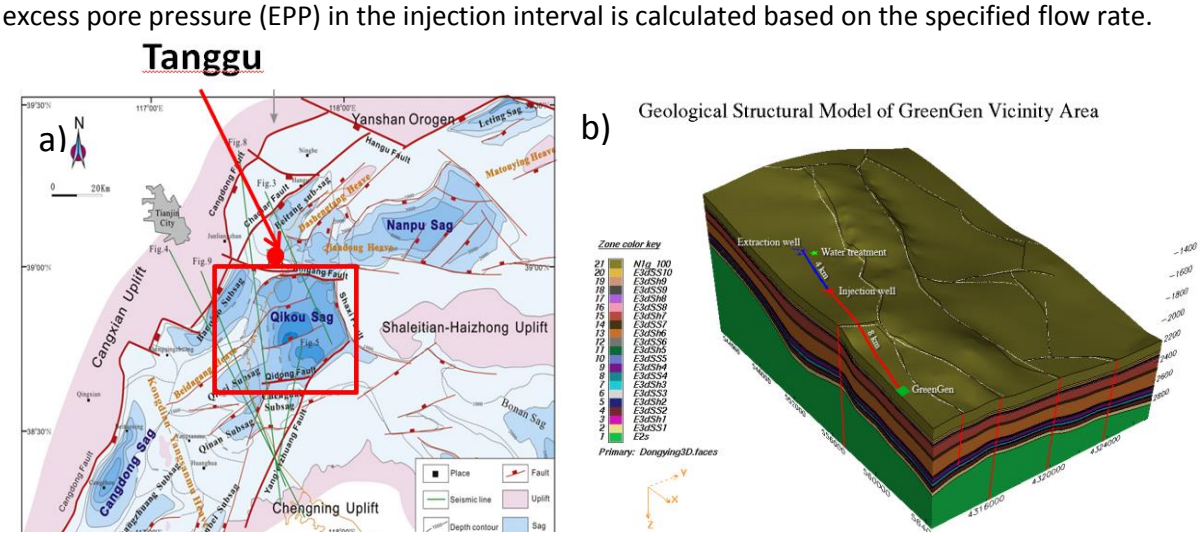


Figure 6: a) Map view of the Bohai Basin area b) Geologic model around the Bin Hai New Area and a hypothetical location of a CO_2 injection and brine extraction well.

Model Parameter Selection

Model parameters are based on extensive literature reviews of two potential regional target reservoirs, the Dongying and Guantao formations (Table 1). Both have beds of high permeability and porosity intercalated with lower permeability layers of mudstone and shale (Yang et al., 2013).

Within CO_2-PENS, normal probability distributions that span the range of data in Table 5 were chosen for the primary parameters of permeability, porosity, and thickness. Due to limited data for the Guantao, it is assumed that permeable layers in this unit are similar in thickness to those found at Well TR21 in the Dongying. Two depths are explored in the simulations, 2000m and 2500m, representing intermediate and deep cases. Deeper plumes will have slightly smaller radius because radius is proportional to the square root of water viscosity divided by CO_2 viscosity times CO_2 density as (Stauffer et al., 2009):

$$r \propto \sqrt{\frac{u_w}{u_c \rho_c}} \tag{3}$$

Table 5: Well TR21 data for productive layers in the Dongying formation (compiled by CERC members Liaosha Song and Tim Carr).

Formation	Depth (m)	Thickness (m)	Porosity (%)	Permeability (mD)
Ed1	1950.1-1963.1	13	27.51	625.25
	1978-1984	6	26.64	480.03
	1989.4-1996.7	7.3	23.35	218.93
Ed2	2073.3-2090.1	16.8	31.41	908.16
	2202.2-2207.6	5.4	31.02	812.55
Ed3	2213.0-2220.0	7	29.98	725.69
	2249.7-2278.8	6.4	25.94	389.88
	2272.3-2278.8	6.5	26.04	406.29
	2284.3-2312.6	28.3	23.41	275.69
	2320.2-2324.9	4.7	26.41	421.98

Figure 7 shows a CO2-PENS dashboard with parameter ranges used in the 2 km deep simulations and a subset of the dashboard for the deeper 2.5 km case. Figure 8 shows the distributions of properties that were sampled for 100 Monte Carlo (MC) realizations in each simulation. Properties that were fixed for all simulations include residual water saturation (0.30) and injector well radius (0.07 m). Dissolution of CO_2 in brine and pore compressibility are not accounted for in these calculations. Further, the ROM was built from multiphase flow simulations where water is being withdrawn from the system along a constant pressure boundary located 20 km from the injectors.

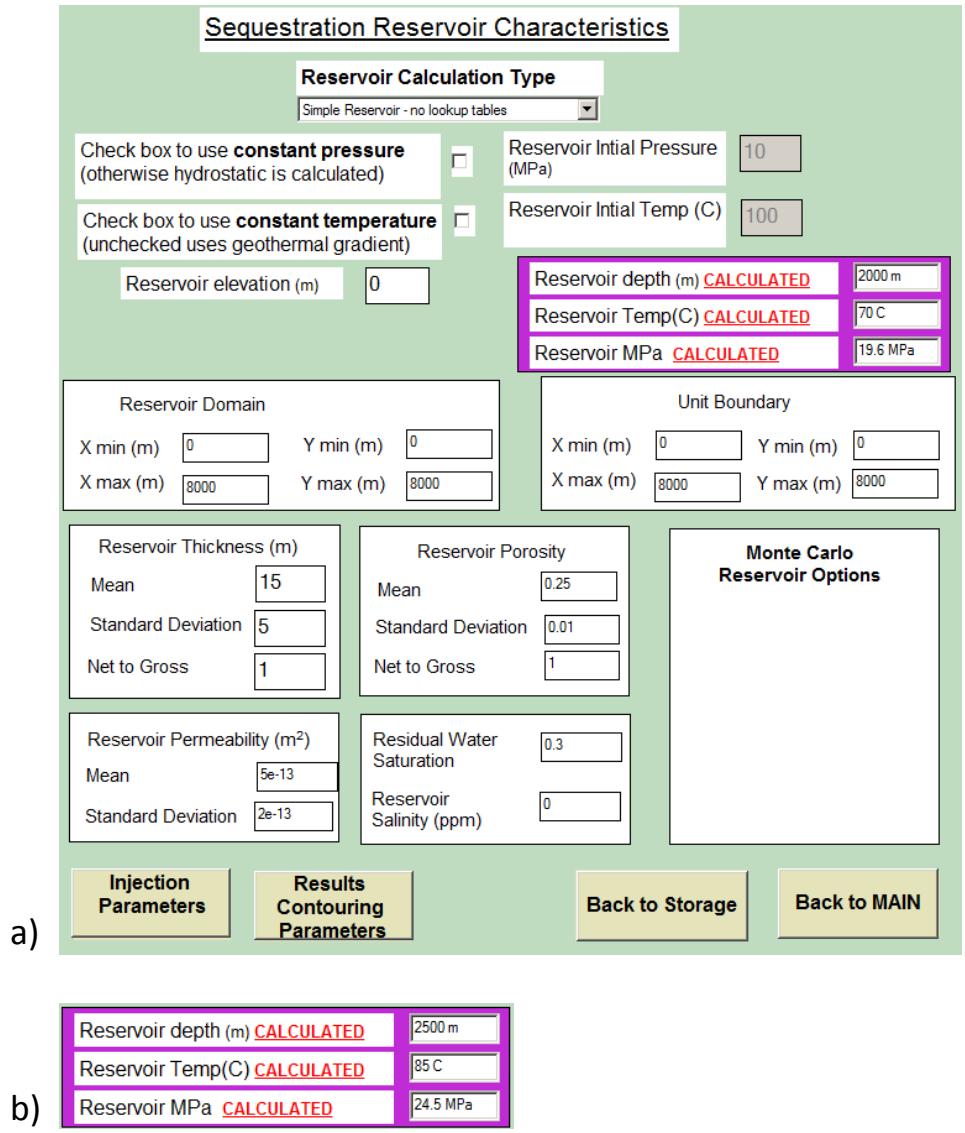


Figure 7: a) CO_2-PENS reservoir dashboard showing input parameters and calculated properties. Grey boxes are not used. b) The only difference for the deeper 2.5 km cases is the initial pressure and temperature.

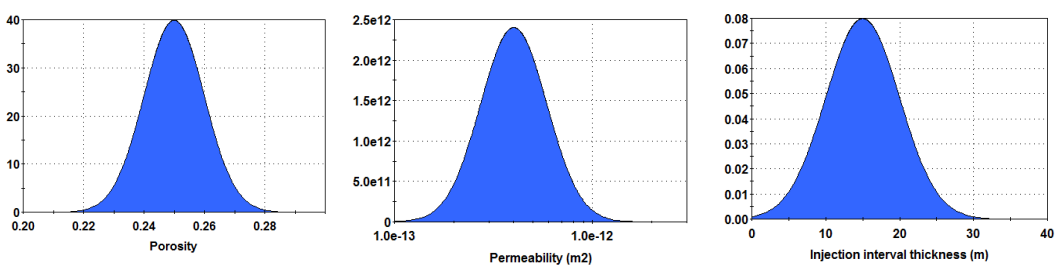


Figure 8: Porosity, permeability, and thickness distributions within CO_2-PENS for target injection layers representing the Guantao and Dongying formations.

Model Results

Table 6 shows the average plume radius and excess pore pressure (EPP) required to achieve the target injection rate in a single well. After one year at the low injection of 0.1 MT/yr, the mean plume radius is only 0.39 km, showing that monitoring wells designed to detect CO_2 breakthrough in this time would need to be placed quite close to the injection well. When injection is increased to 1 MT/yr, the plume at one year averages 1.22 km. Average values give a good sense of differences between simulated cases. However, because of uncertainty in parameters for a given case, variability in

plume radius changes by a significant amount for each of the 100 MC realizations of a given case. Figure 4 shows how the plume radius varies with both layer thickness and porosity for the case of 2.5 km depth, 0.1 MT/yr, and 10 years of injection. The right side of Figure 9 rotates the 3D view to show the strong inverse correlation between layer thickness and plume radius. As predicted by Eq. 3, average plume radius decreases (3.85 km to 3.48 km) as depth increases (2 km to 2.5 km) for the case of 1 MT/yr for 10 years. A similar decrease in radius is seen for the 0.1 MT/yr case.

Table 6: Plume radius and injectivity results

Depth (km)	Injection period (years)	Injection rate (MT/yr)	Mean radius (km)	Mean EPP (MPa)
2	1	0.1	0.39	0.24
2	1	1.0	1.22	1.94
2	10	0.1	1.22	0.25
2	10	1.0	3.85	2.03
2.5	10	0.1	1.10	0.22
2.5	10	1.0	3.48	1.73

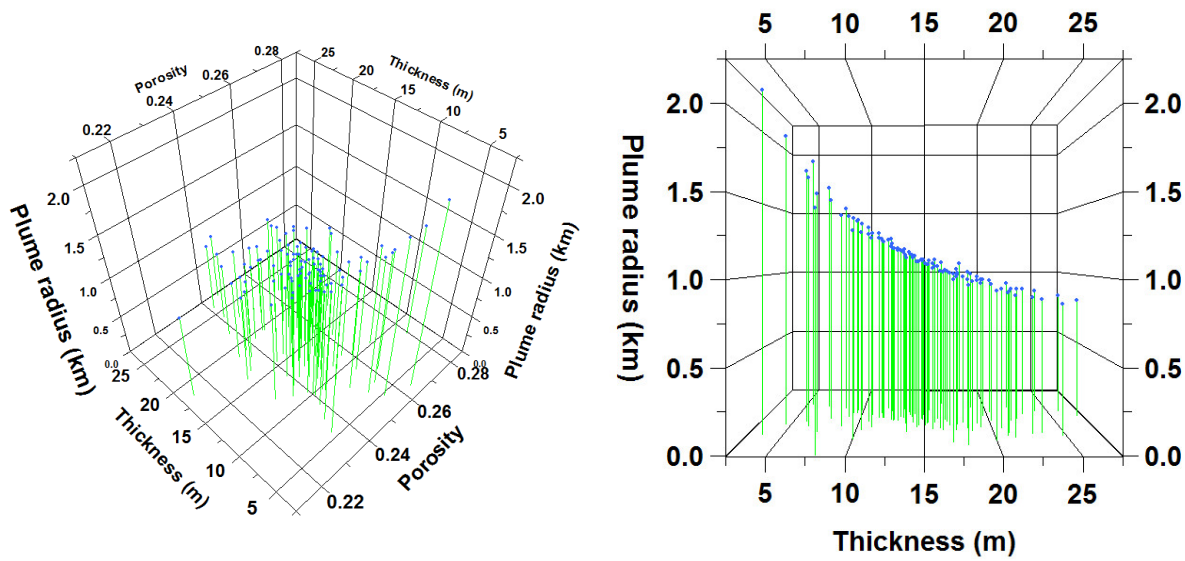


Figure 9: Plume radius variation with thickness and porosity (0.1 MT/yr, 2.5km deep, 10 year injection)

Histograms for EPP and plume radius for the two cases are shown in Figure 10. Clearly there are cases where injection of 1 MT/yr into one layer results in very high EPP (> 4.0 MPa). High EPP is of concern due to the possibility of either hydrofracture or induced seismicity. A simple calculation of lithostatic stress relative to hydrostatic (using 25% porosity and a formation density of 2650 kg/m^3) yields Figure 11A, where at 2.5 km depth a low estimate of hydrofracture (65% of lithostatic) is 10.6 MPa of EPP. However, overpressure is seen in some formations around Tianjin (Figure 6B) and care will need to be taken to measure in-situ pressure conditions before setting injection rates as high as 1 MT/yr. In fact, Figure 11B shows that at 3200 m depth, pressure is within only 2Mpa of the 1.6 pressure coefficient line (approximately 0.7*lithostatic). For 0.1 MT/yr there is low probability of exceeding 0.65*lithostatic, with most EPP values well below 0.5 MPa (Figure 10C). Because of high permeabilities found at this site, a single well should be able to inject up to 1 MT/yr, especially if background pressure is near hydrostatic and the injection well is screened in a high permeability layer with thickness greater than 10 m.

Sensitivity analysis of the parameters shows that injection layer thickness has the most impact on plume radius variability (65%), while porosity and permeability provide much smaller contributions to uncertainty (7.5% and 4.3% respectively). Excess pore pressure is controlled by a combination of thickness and permeability (37.2% and 33.5% respectively), with porosity variation having little impact (1.2%). Figure 12A shows the variability in injection EPP as a function of permeability and thickness for 100 realizations (1 MT/yr, 10yrs, 2km). The largest injection EPP of 8.24 MPa results from a combination of low thickness (5.6 m) and relatively low permeability (250 mD). Figure 7B shows the strong negative correlation between injection EPP and thickness of the injection interval for the same case.

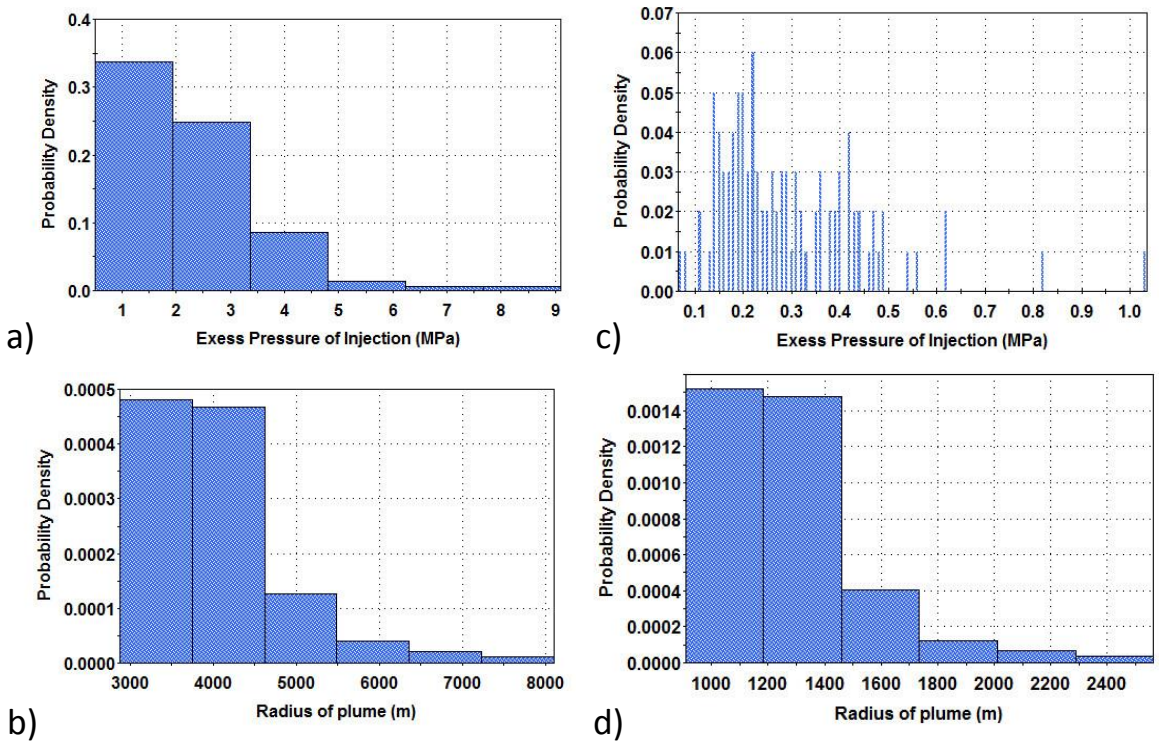


Figure 10: EPP and plume radius histograms for a,b) 1 MT/yr, 10yrs, 2km and c,d) 0.1 MT/yr, 10yrs, 2km

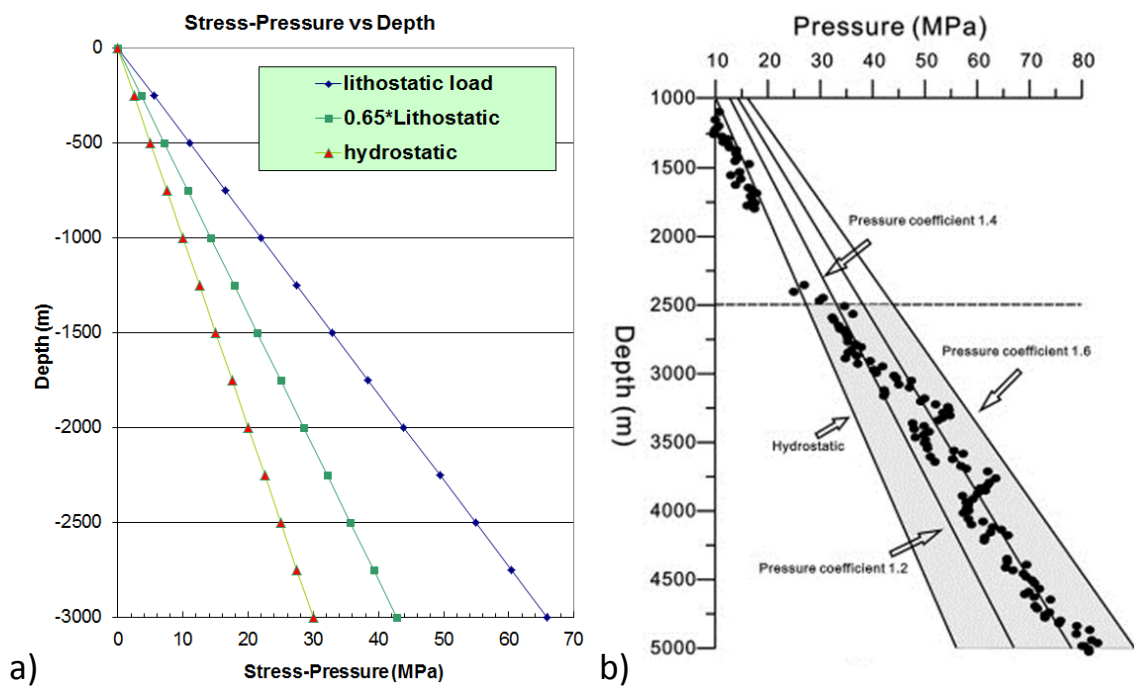


Figure 11: a) Lithostatic stress relative to hydrostatic and 65% of lithostatic failure line and b) Pressure data from the Qikou Sag near the target injection site.

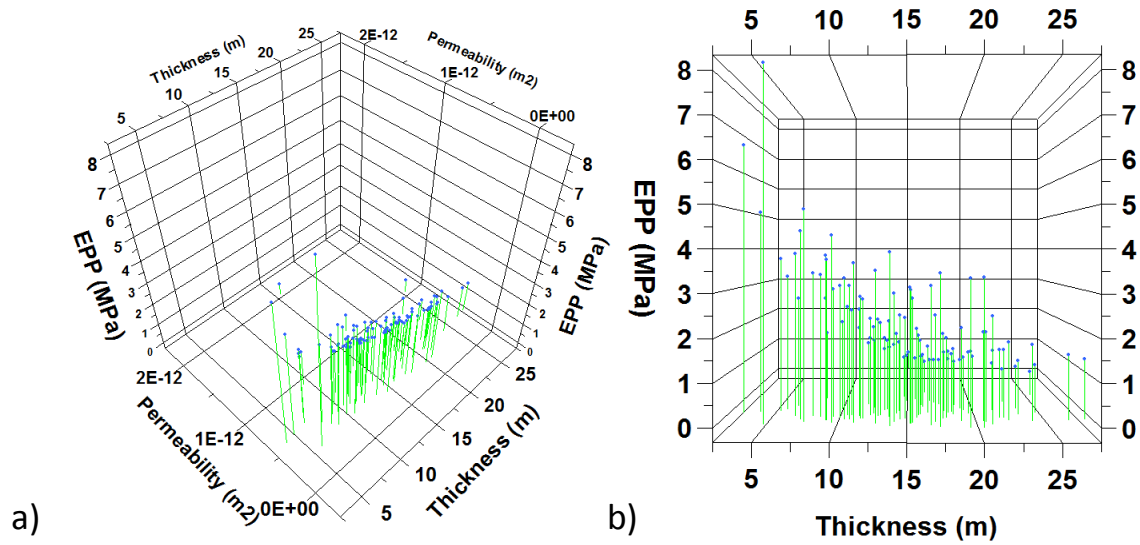


Figure 12: Injection EPP variability versus thickness and permeability

Conclusions

Reduced-order calculations of injectivity and plume radius support the viability of the Guantao and Dongying formations as CO_2 injection reservoirs. Low excess pore pressure is required to inject up to 1 MT/yr in many cases, implying that a single well will be required to inject CO_2 from the GreenGen facility. Plume radius for the initial injection at 0.1 MT/yr is likely to be quite small (0.39 km) after one year. If a project goal is to detect breakthrough within this time, a monitoring well will need to be placed close to the injection well. Brine production could likely take place within 2 km from the injector and not encounter breakthrough at 0.1 MT/yr injected for 10 years. For 1 MT/yr, the one year average plume radius is on order of 1.2 km, suggesting that a monitoring well could be placed farther from the injector. The brine production well for the 1 MT/yr case would likely need to be located approximately 6-8 km from the injection well to ensure limited breakthrough. These calculations are conservative because the team does not include reservoir management strategies such as pre-injection brine production to lower pressures, multiple sets of injection and production wells, or heterogeneity in the high permeability layers. More detailed analysis will only be possible when higher resolution site data become available, such as 3-D seismic density maps and pump tests on existing geothermal and/or new test wells.

GEOLOGICAL CONSIDERATIONS IN DEVELOPING A RESERVOIR MANAGEMENT STRATEGY

The Bohai Bay Basin, China is a northeast-southwest trending transtensional basin. It is composed of numerous, smaller highlands and subbasins which developed between several generations of major and minor extensional, oblique, and strike slip faults. The Bohai Bay Basin is a textbook example of a negative flower structure; a multitude of juxtaposed half grabens and grabens bound by massive, regional strike slip faults.

For this study the Dongying formation will be considered as the potential injection formation. The upper portion of the Dongying formation is comprised of fluvial-deltaic deposits. The middle illustrates a transition to deeper water, and associated deep lacustrine, delta fan, and sub lacustrine fan deposits. The lower portion is comprised of shoreline lake deposits (Dong et al., 2011, Zhang et al., 2008). The transgressive sequence during Lower Dongying formation resulted in a higher deposition rate, and consequently is over pressured (Li Chunguang, 2006). The reservoir pressure of the middle and upper Dongying is slightly over or normal pressured (Zhang et al., 2013). The Dongying formation at the Dagang Oil Field (where GreenGen Plant is located) is comprised of interbedded grayish green mudstone, green shale, and fine grain to coarse grain sandstone. The thickness of the Dongying formation ranges from 100 m to 600 m across the Huanghua Depression. At the proposed injection location, the thickness of the Dongying Formation is roughly 400 m. There are 120 m of sandstone with porosity ranging from 23% and 31%, and permeability from 200 md to 900 md.

Water quality data from the Dongying formation are sparse. However detailed water quality results are provided by Minnissale et al. (2008) for the Tertiary aquifer system. Samples collected from the Lower Tertiary aquifer system, may be representative of a first order approximation of the water quality of the Dongying formation. These results indicate that salinity ranges in Dongying formation in the study area range from 750 mg/L to 2,500 mg/L. Water type is sodium-bicarbonate-chloride with an alkaline to neutral pH (6.8 to 8.1). Dissolved minor and trace elements are generally less

than 5µg/l. No information is given for dissolved organics, volatile organics, or radio nuclides. Dissolved gas compositions are measured to be greater than 90% methane with minor concentrations of CO_2 and N_2.

Preliminary Geologic Model

A 3D structural model for the Tianjin GreenGen vicinity area was generated on the basis of available data. The GreenGen project is located at the southeast corner of the model. The fault block at the southwest of the model could be used for the CO_2 injection and reservoir fluid extraction. A CO_2 injection well is located 8 km northwest of the GreenGen Plant. A reservoir fluid extraction well is located 4 km away from the injection well in the up dip direction. This model could be used in the next phase of study for investigation of pressure evolution, storage capacity, injectivity, and necessary amount of fluid extraction during the CO_2 injection.

Based on existing structural examinations of the study area, a crucial consideration for potential CO_2 injection and storage site is the proximity and nature of Neogene-Quaternary faults. There are two major faults that bound the study area, Cangdong on the west and Haihe on the north. The Cangdong trends north-northeast and dips south-southwest and cuts into the Neogene Minghuazhen Formation (Yang et al., 2013). The Cangdong is rooted into the Oligocene Dongying Formation (Yang et al., 2013). Strata to the west of the fault are Precambrian and Paleozoic, while to the east of it the strata are mainly Mesozoic and Cenozoic. The Haihe fault strikes northwest-west and dips south-southeast, cutting into the Minghuazhen Formation 80-120 m (Yang et al., 2013).

The Dongying formation is divided into 10 sandstone layers interlayered with 9 mudstone/shale layers. Note that a 188 m layer of mud/shale (Figure 13, Layers 6 and 7) could serve as potential confining layers for CO_2 containment. At this injection location, a CO_2 plume with 1.5 km radius (the estimated CO_2 plume size for 50 million tons), would not likely reach the major faults in any direction.

The tertiary aquifers in areas adjacent to the faults express a relatively higher total dissolved solids (TDS) concentration and the Paleozoic aquifers show a relatively lower TDS concentration. This has been interpreted to indicate unconfined aquifers in the faulted areas (Yang et al., 2013). Further evidence by isotope age relationships, indicating that water near the fault is younger (Yang et al., 3013). In contrast, many of the regional faults in the area also serve as fault traps in younger strata. The transmissivities of the faults in the study area present a critical unknown that should be addressed in subsequent work.

The estimated salinities of the formation fluids are low, indicating that only minimal treatment would be required for agricultural and industrial use. The low concentrations of dissolved minor and trace elements also indicate that mineral extraction is not likely a possibility from these fluids. However there is some indication that Dongying reservoir fluids may be a candidate for low-temperature geothermal development.

Geological Structural Model of GreenGen Vicinity Area

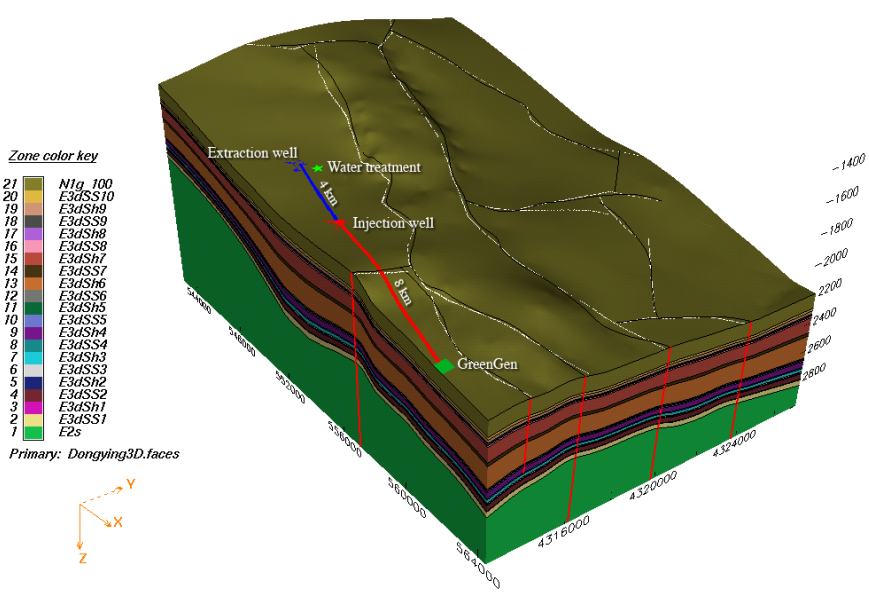


Figure 13: Geologic model around the Bin Hai New Area and a hypothetical location of a CO2 injection and brine extraction well

Recommendations

On the basis of this preliminary assessment, the Dongying Formation looks to be an appealing candidate for further study as a potential CO_2 storage formation for the Huaneng's Tainjin GreenGen facility. This initial assessment has identified areas of critical unknowns to be address within a feasibility study of the area.

Recommendations for a detailed feasibility study include:

1) Acquire robust databases for the target storage domains and adjacent areas. Recommended data sources included seismic data with customized processing, and petrophysical well data including diverse log suites, cores, a vertical seismic profile (VSP) survey, in-bore testing (drill stem test, injection, and rock property testing), and available geochemical data.
2) Obtain detailed water quality data from the Dongying Formation in the area of review. It is important to note that specific water quality data from the Dongying Formation, and preferably from the injection intervals are needed to determine a specific reservoir management plan. These data at minimum should include: pH, temperature, major and minor elements, and oil and grease concentrations
3) Use these data to generate a detailed 3-D property model used for numerical simulations and performance assessments.
4) Using the numerical simulations and performance assessments, evaluate a range of CO_2 injection/storage scenarios for target reservoir intervals to determine if pressure management is required to maintain the integrity of the storage domain, or to ensure domain boundaries, evaluate the plume boundaries, volume, and rate of formation fluid removal necessary for low-risk storage.
5) Detailed examination and identification of fault types within the study area would help to subjugate risk and reduce uncertainty. Also of critical importance for determining structural response to injected fluids would be to test the fracture and slip potential of Neogene-Quaternary faults. As many of these faults bound mature oilfields, it is likely these data has already been obtained, and would be necessary for determining conservative pressure estimates and reduce the risk of failure during injection.
6) Design water production configuration. Define water production volumes and rates based on reservoir parameters developed in the 3-D property model. Plans should include transportation to a treatment facility, and options for water treatment technology.

CONCEPTUAL BRINE TREATMENT AND HANDLING STRATEGY

Literature search findings showed more comprehensive chemical characterizations of water from Guantao formation than those for water from Dongying formation. The reported water quality characteristics are summarized in the following and compared to the Chinese national water quality standards for industrial uses of urban recycling water (Table 8).

Guantao formation water

Water samples collected from the Guantao formation Ng-III aquifer are of HCO_3• Cl–Na or Cl•HCO_3–Na type (Pang et al., 2012). The total dissolved solids (TDS) concentration ranged from 1.15 g/L to 1.65 g/L, consistently higher than the TDS standard for industrial uses (1 g/L). Wellhead temperatures measured were mostly between 50 °C and 70 °C. *In-situ* pH indicates that the water was neutral to alkaline with an average pH of 7.7, falling in the range of industrial uses standards. Bicarbonate (HCO_3^-), a major contributor to alkalinity, had concentrations ranging from 445 to 670 mg/L, which consistently exceeded the alkalinity standard (350 mg/L $CaCO_3$, Table 1).

Sulfate concentrations (181 – 233 mg/L, with one sample reaching 320 mg/L) were generally lower than its standards for the industrial uses (600 or 250 mg/L). Two major water hardness contributing cations (i.e., Ca and Mg) were relatively low compared to the total hardness standard (350 mg/L $CaCO_3$). Chloride concentrations (221 – 360 mg/L) were mostly above its standard (250 mg/L) and in some applications would require removal.

Silica (SiO_2) can cause fouling on surfaces of heat exchangers and other devices at power plants and its concentrations ranged between 30 – 50 mg/L in the Guantao formation water, which were mostly lower than the standard for cooling (50 mg/L). However, the concentrations consistently exceeded the boiler water standard (30 mg/L) and require treatment.

Dongying formation water

Information on Dongying formation water chemistry was much more limited than for the Guantao formation. The production of a single well from in the formation was about 40 m^3/h, with water temperature 73°C, and salinity close to 3 g/L. The water chemistry type is Cl • HCO_3-Na, the value of rNa/rCl is about 1.47 (Lin et al., 2010). Another study reported

TDS concentrations ranged from ~4 – 23.7 g/L (Xu et al., 2010). All these results indicated the need for desalination of the formation water to meet the TDS standard for industrial uses.

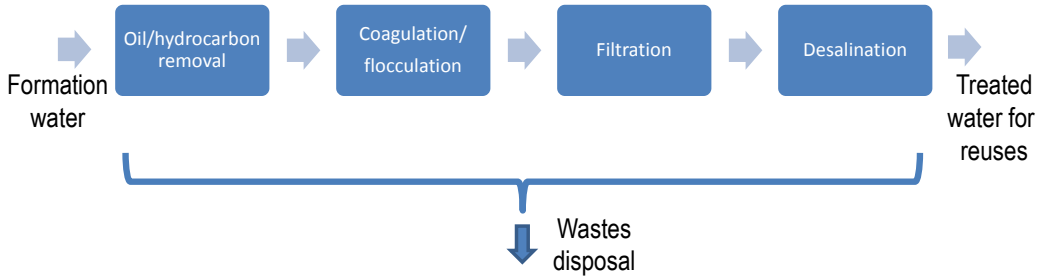
Given that the formations are rich in hydrocarbon, it is likely that the formation waters contain oil and petroleum based compounds. This would require additional treatment for removing organic matters to meet the standard for petroleum, 1 mg/L.

Table 8: Water quality standards for industrial reuses of urban recycling water.

	Cooling		Washing	Boiler water	Process/ products
	Once-through	Recirculation			
pH	6.5-9.0	6.5-8.5	6.5-9.0	6.5-8.5	6.5-8.5
Chromaticity	≤30	≤30	≤30	≤30	≤30
Suspended solids (mg/L)	≤30		≤30		
Turbidity (NTU)		≤5		≤5	≤5
Total hardness (mg/L CaCO3)	≤450	≤450	≤450	≤450	≤450
Alkalinity (mg/L CaCO3)	≤350	≤350	≤350	≤350	≤350
TDS (mg/L)	≤1,000	≤1,000	≤1,000	≤1,000	≤1,000
DO (mg/L)					
BOD5 (mg/L)	≤30	≤10	≤30	≤10	≤10
COD (mg/L)		≤60		≤60	≤60
NH3 (mg N/L)		≤10		≤10	≤10
Total P (mg/L)		≤1		≤1	≤1
Sulfate (mg/L)	≤600	≤250	≤250	≤250	≤250
Chloride (mg/L)	≤250	≤250	≤250	≤250	≤250
Residual chlorine (mg/L)	≥0.05	≥0.05	≥0.05	≥0.05	≥0.05
SiO2 (mg/L)	≤50	≤50		≤30	≤30
Fe (mg/L)		≤0.3	≤0.3	≤0.3	≤0.3
Mn (mg/L)		≤0.1	≤0.1	≤0.1	≤0.1
Anionic surfactants (mg/L)		≤0.5		≤0.5	≤0.5
Petroleum (mg/L)		≤1		≤1	≤1
Total coliforms (#/L)	≤2,000	≤2,000	≤2,000	≤2,000	≤2,000

Proposed strategy for handling the brine water and waste disposal

Given the limited information on formation waters, a general strategy for turning the formation waters into a regional water resource for industrial uses such as those at thermoelectric power plants is proposed. The strategy includes treatment of the formation waters to meet the national water reuse standards for industrial uses, properly locating the treatment site, transporting the treated water, and disposal of the wastes from the treatment process. A conceptual treatment process illustrated as below:



The first treatment stage is to remove oil and petroleum based compounds from water using oil/liquid separator (gravitation separation) or adsorptive method. Coagulation/flocculation is to remove fine colloidal particles and chemicals

such as silica, followed by filtration to remove flocculated aggregates. Desalination is essential to lower TDS and salt content for reuse of the water at power plants.

CONCEPTUAL COST/PERFORMANCE MODEL- WATER TREATMENT

Extraction of water during CO_2 carbon storage operations provides a mechanism for reducing the risks associated with CO_2 storage by controlling CO_2 movement and providing pressure control. At the same time, water extraction creates a water resource for human use. Understanding the goals for water use at the surface will dictate the treatment processes, treatment train design, and costs for creating a useable water stream. During a preliminary system design phase, site-specific information may not be available and so literature data must be used to assess treatment train processes and costs. Note that all cost values shown are in U.S. Dollars (USD). All model values and results are for cubic meters (m^3) of water unless otherwise stated.

CO_2-PENS Water Treatment Module (CO_2-PENS WTM)

The water treatment system must be linked to the CO_2 storage system operations, in order to correctly evaluate the effects of different volumes, pressures, temperatures, and extracted water quality on treatment train process choices and costs. The WTM was developed using the GoldSim© platform (GoldSim© Technology Group 2010, Sullivan et al., 2013). GoldSim© is used to develop analysis models that perform multi-realization, probabilistic simulations. A FORTRAN code captures the logic of treatment process selection and is linked within GoldSim©. GoldSim© utilizes custom data elements for input of user-specified parameters including stochastic distributions. The WTM captures all decision points; both stochastic range and constant data input values. Figure 14 shows a model schematic diagram including the various sub-modules that calculate final costs and volumes.

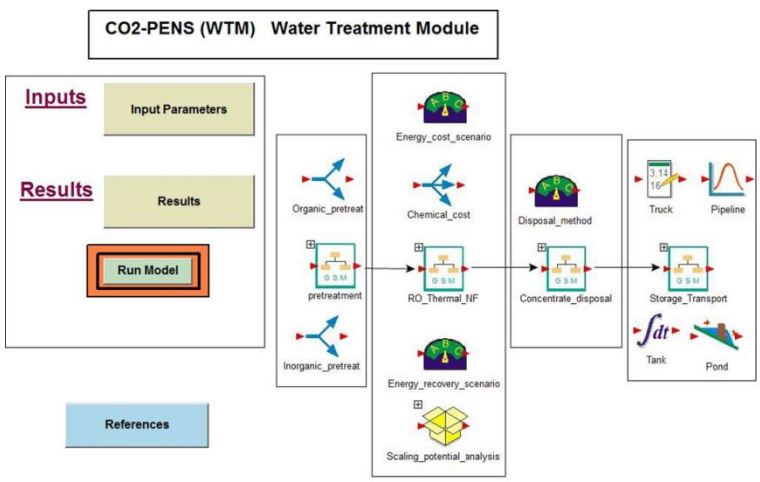


Figure 14: CO_2-PENS WTM Model Schematic

Note that the CO_2-PENS WTM was developed using data, costs, and logic associated with systems found in the United States. This is particularly important for understanding the results for different disposal scenarios. Disposal of saline concentrate from water treatment is regulated under various discharge permits. Deep well injection, for example, is regulated by the U.S. Environmental Protection Agency Underground Injection Control Program (http://water.epa.gov/type/groundwater/uic/wells.cfm) and the type of well choice is influenced by the classification of the water source. For the WTM, a key difference is the distinction between oil and gas "produced" water, versus wastewaters from other sources. Produced water may only be disposed via a Class II injection well in the U.S., whereas other wastewaters may be disposed via Class I or Class V wells depending upon the source and potential risk to the environment. The WTM model makes this choice for the user once the user inputs the type of water to be treated (produced or not produced). It is anticipated that future uses of the model may incorporate scenarios and logic for different countries and regulatory perspectives.

Model Parameter Selection

Model parameters were based on extensive literature reviews of two potential regional target reservoirs, the Dongying and the Guantao (discussed elsewhere in this report). Both formations have relatively low salinities and low concentrations of scale-forming minerals including divalent-ion carbonates and sulfates and, thus, are good candidates for relatively economical water treatment. Ultimately the Guantao was chosen for the primary simulations, although several scenarios including salinity and temperature ranges for the Dongying were run to illustrate the effect of higher salinity on the model

results. Scenario choices are shown in Table 9. The approximate volume expected from an initial pilot test of the system is 400 m^3/day. This volume is low compared to volumes treated by most water treatment plants; typical plants are often built to handle over 37,850 m^3/d (10 Mgal/d).

Table 9: Scenario Choices for Preliminary Cost Assessment.

Formation	Salinity Range (mg/L TDS)	Temperature Range (°C)	Produced Water Yes/No	Scenario ID-Product water quality
Guantao	716-1760	40-73	Yes	Case 7a-Boiler Water
Guantao	716-1760	40-73	no	Case 8a-Boiler Water
Guantao	716-1760	40-73	Yes	Case 7b-Cooling Water
Guantao	716-1760	40-73	no	Case 8b-Cooling Water
Guantao	716-1760	40-73	no	Case 8c-Cooling Water with organic pretreatment
Dongying	1300-16000	10-85	Yes	Case 1a-Boiler Water
Dongying	1300-16000	10-85	no	Case 2a-Boiler Water
Dongying	1300-16000	10-85	Yes	Case 1b-Cooling Water
Dongying	1300-16000	10-85	no	Case 2b-Cooling Water
Dongying	1300-16000	10-85	no	Case 2c-Cooling Water with organic pretreatment

The calculations and results include uncertainty in some parameters to show possible variations in costs. Electricity costs are assumed to be $0.07/kW hr. These calculations do not include costs related to borehole construction or compression of CO_2. For the Guantao Formation, CO_2 transport costs by truck for 400m^3/day (i.e. ~ 0.15 MT/yr) from GreenGen to the injection site is included. Note that increased degradation of reverse-osmosis (RO) membranes can occur at the higher temperatures evaluated (>45°C), and so treatment in this range may incur greater membrane replacement (O&M) costs than calculated here.

Table 10 lists selected key model features and a description of the selection process for each feature.

Table 10: Listing of selected model features.

Key Features	CO_2-PENS WTM
Cost of Electric Power	User-selected variable, no plant –type assumptions
Pre- and post-treatments	User-selected variable or model assists
RO Energy Recovery	User-selected variable methods; can be omitted.
Economies of Scale	Stochastic ranges from literature values with scaling algorithm
Disposal	Multiple methods, stochastic ranges. User-selected parameters guide model choices.
Transportation	Pipeline and/or Trucking, user-selected variable type and distances, stochastic ranges for costs based upon literature.
Storage	Model Selected, Tank or Pond, depending upon calculated storage volumes. Also can be user-selected.

Model Results-Costs and Sensitivity Analysis

Table 11 shows the cost average and standard deviation for each possible treatment and disposal method for cases 8a, 8b, and 8c. Figures 15, 16, and 17 show the plotted results. The costs include water treatment (RO and thermal methods) cost, disposal cost (depends on type of water, there are several different possible disposal methods), transport and storage cost.

Table 11: Results for non-produced water cases.

Case (categorized by disposal method)	Average Cost (USD/m^3 incoming water)	Standard Deviation
8a-reuse	2.37	1.02
8a-surface discharge	3.12	1.47
8a-sewer	3.18	1.46
8a-ocean	2.55	0.26
8a-class V well	2.56	0.27
8a-zero-liquid discharge	2.59	0.28
8b-reuse	2.33	0.70
8b-surface discharge	2.92	1.21
8b-sewer	2.96	1.22
8b-ocean	2.27	0.54
8b-class V well	2.28	0.54
8b-zero-liquid discharge	2.30	0.56
8c-reuse	3.87	1.85
8c-surface discharge	4.45	2.23
8c-sewer	4.50	2.25
8c-ocean	3.85	1.69
8c-class V well	3.86	1.70
8c-zero-liquid discharge	3.88	1.71

Costs below T=45°C represent mostly (RO) costs. In Figure 15 (case 8a), the treatment goal is so low (150 mg/L TDS) that another membrane process, nanofiltration (NF) will not achieve the goal based on the water chemistry; RO is needed to meet this concentration goal for membrane system permeate, 15% of treatment use RO method, 85% use thermal method. All of the Guantao scenarios have a number of potential disposal options, mostly because the rejected concentrate is within reasonable salinity ranges for (<3,000 mg/L) surface disposal.

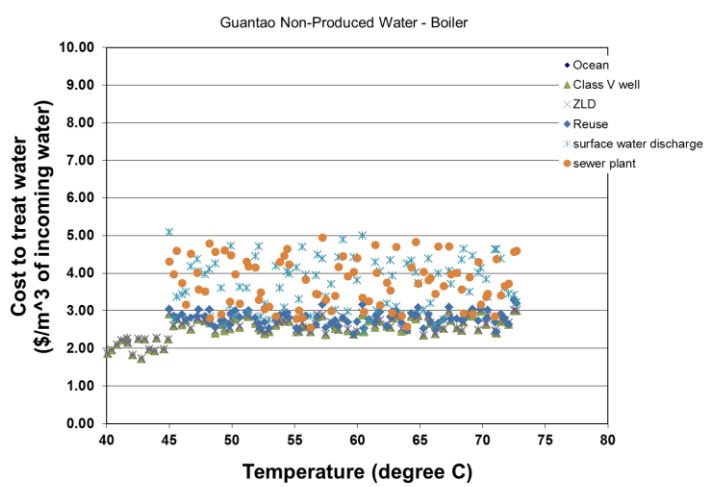


Figure 15: Case 8a, Guantao Fm., non-produced water scenario for Boiler water treatment goal.

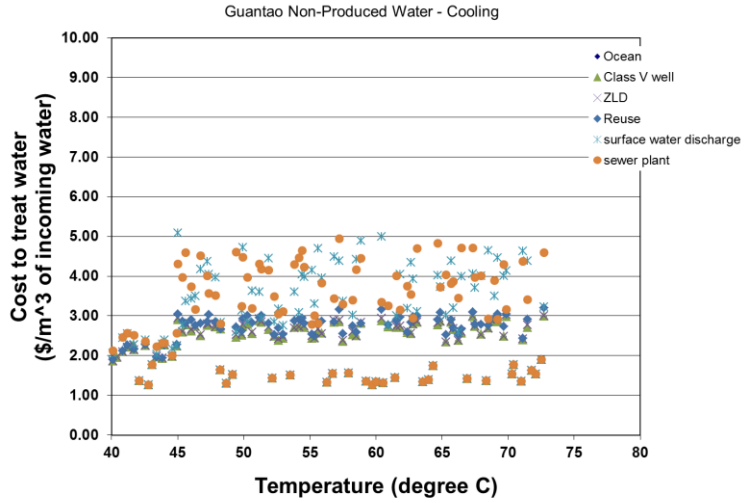


Figure 16: Case 8b, Guantao Fm., non-produced water scenario for cooling water treatment goal.

In Figure 16 (case 8b), the cooling water treatment goal of 1000 mg/L is high enough that 12% of treatment use RO, 61% use thermal, and the rest 27% is clean enough relative to the treatment goal so it do not even need treatment.

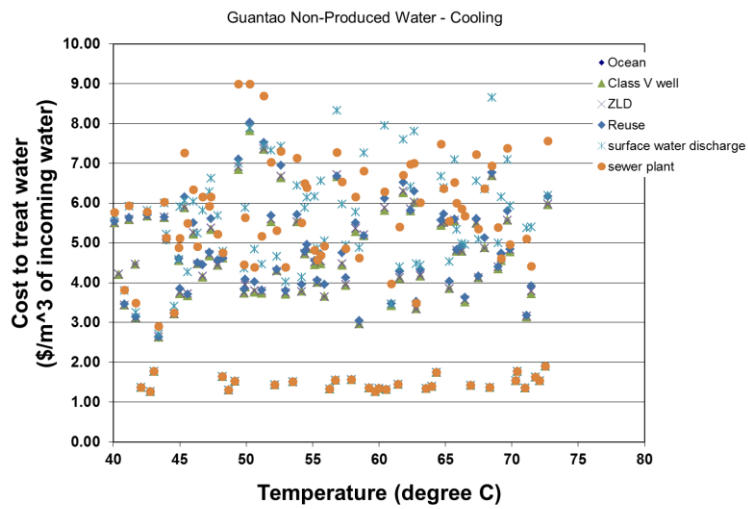


Figure 17: Case 8c, Guantao Fm., non-produced water scenario for cooling water treatment goal with organic pretreatment included.

In Figure 17, the cost range is wider because of the addition of organic pretreatment. We use a stochastic distribution of costs to incorporate the wide range of potential treatment options that might be needed.

The Guantao Fm. is identified as a geothermal formation, as opposed to the Dongying Fm. which is identified as an oil and gas producing formation. The WTM includes costs for Class II well disposal in the produced water scenarios. These disposal costs are documented in the literature to range from \$0.06 to \$63.00 per m^3 of water disposed, contributing three orders of magnitude variation to these costs. This result is based upon U.S. disposal cost ranges and thus may not be applicable to other locations outside of the U.S. The results do show the effect that high disposal costs can have on the cost distribution.

A sensitivity analysis for the cooling scenarios 8b and 8c was conducted to show the relative importance of the input parameters on final costs. For scenario 8b (Figure 18), water supply quality (TDS), truck transportation rates, and tank storage rates are indicated as being most important to costs, followed by parameters related to pretreatment such as antiscalent costs and feed pH. Transportation distances also have some significance, as well.

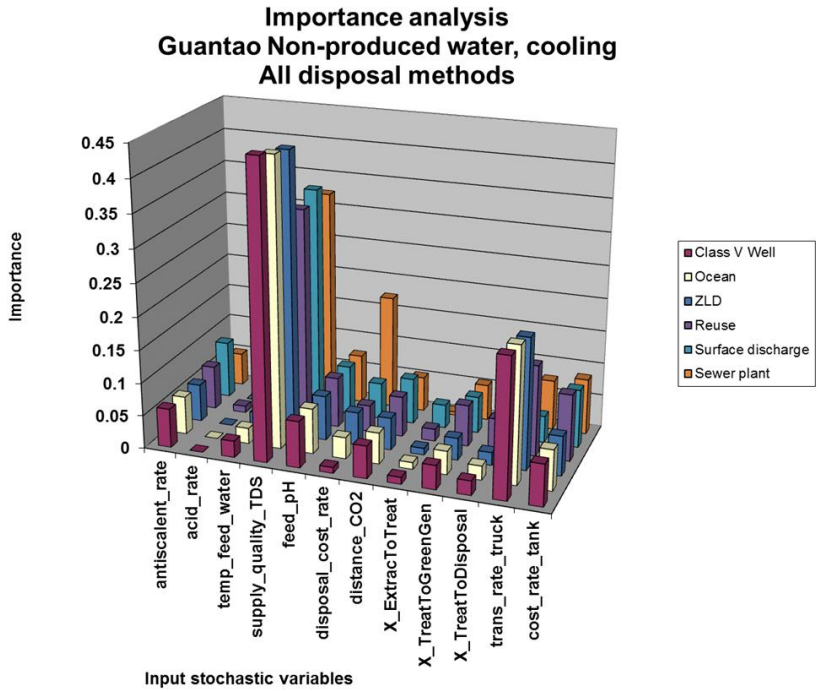


Figure 18: Case 8b, importance analysis for cooling treatment goal stochastic parameters.

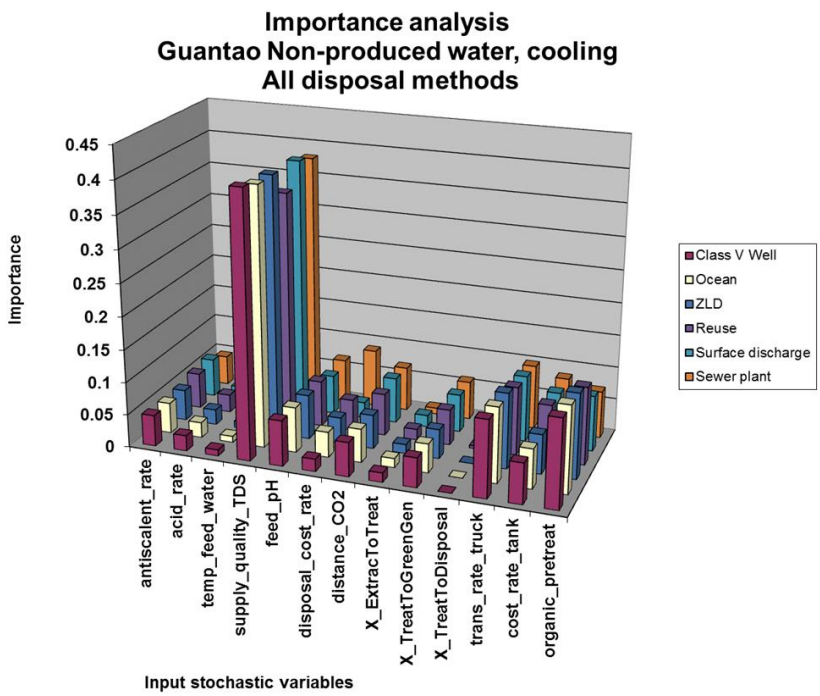


Figure 19: Case 8c, importance analysis for cooling treatment goal stochastic parameters with organic pretreatment.

For scenario 8c (Figure 19), the case with organic pretreatment included, a similar distribution of relative importance factors is seen. Supply quality TDS is still the most important cost factor, followed by truck transportation rate, and organic pretreatment. Here the large cost variance of the latter increases its relative importance to other treatment factors, as expected.

Discussion

The low influent volume (Q_{in}=400 m^3/d) for this test case may result in higher costs because economies of scale cannot be effectively included for transportation, storage, and other processes. However, the costs evaluated are relatively low

compared to other site evaluations for higher salinity waters and indicate that treatment is a feasible option for this location (Sullivan et al. 2013). This model shows stochastic best estimates of cost ranges. More and better field data for a specific site will allow for more accurate cost evaluations using rigorous engineering-based models.

Expected recoveries from various treatments is listed in Table 12. Recoveries are quite good because the influent water quality is of relatively low salinity.

Table 12: Recovery rate

Case	Mean (%)	Standard Deviation
8a (produced water, boiler)	92.78	2.75
8b (non-produced water, cooling)	95.25	4.66
8c (non-produced water, cooling, organic pretreatment)	95.25	4.66

Organic pretreatment was evaluated for one of the Guantao Fm. scenarios, to indicate the effect that this step has on overall costs. While the Guantao Fm. is not identified as an oil and gas producing formation, it was used as an illustrative case. If residual organic carbon is found in the extracted water, then organic pretreatment may need to be considered, particularly for membrane treatment methods, or if volatile emissions from the treatment process are a concern (e.g., benzene, toluene, ethylbenzene, xylenes). Figure 17 indicates that costs could increase by as much as \$2.00-\$4.00/m^3 if organic pretreatment is needed.

There are multiple pathways for concentrate (reject) disposal or use, as shown in the different model scenarios. While the model results are based upon discharge limitations for the U.S. and injection well criteria from the U.S. Environmental Protection Agency, the model may need to be modified to include specific discharge or injection rules and costs for international use. The Guantao Fm. chemistry data indicates a low level of influent salinity, and, thus, concentrate reject will also not be very high in salinity and likely can be directly discharged to surface water, sewer, or the ocean. This is the most economical method of concentrate disposal and will keep treatment costs very low as long as expensive transportation methods are not needed.

Some concentrate disposal methods have very large standard deviations in reported costs. We take reported capital and O&M costs and amortize these over 25 years and 6% interest, divided by a per-year volume for the plant to determine the cost/m^3 for each method; if no capital and operations and maintenance (O&M) costs are reported we use cost/volume reported data as is. For example, zero-liquid discharge (ZLD) literature costs range from \$0.04/m^3 to \$20.00/m^3, with a median cost of \$5.84/m^3 and a standard deviation of \$6.35/m^3 (Juby, 2000; Boysen, 2003; DiNatale, Kaunisto, & Brown, 2010; Kim, 2011). At this time, the team used a normal distribution to apply stochastic ZLD disposal costs. Costs for large systems or mineral-specific recovery systems trend toward the high end of the scale (~\$7.00-20.00/m^3), while new, smaller-scale units that are transportable are much more cost-effective, in the range of \$2.00-4.00/m^3 (David Delasanta, Thermo Energy Corporation, personal communication to ejsg, July, 2014). As the team further defines potential disposal scenarios for international use, then these costs will be refined, and alternative cost distributions can be applied.

The cost for transport CO_2 to injection site is calculated in Dongying Formation non-produced water scenario, the average cost is \$0.612/m^3. The CO_2 density under the compressed liquid condition (-30 C at 1.7 MPa) is 1076 kg/m^3, which is very close to the water density (APEC, 2013; Isothermal Properties for Carbon Dioxide). Therefore it is reasonable in this calculation assuming the CO_2 volume transported is the same as volume of water to be treated.

Potential uses for treated waters include industrial uses, such as the boiler water and cooling water treatment goals shown in this report, municipal, or agricultural use. Some limiting factors for these uses include a boron concentration of 5 mg/L (15 mg/L as borate ion). Boron is difficult to remove even with membrane processes; thermal processes may be more effective to reduce this below lower agricultural tolerance levels (1-15 mg/L).

Further work will need to be done to better understand the site configuration, transportation distances, and disposal options and costs for a site-scale evaluation. It is critical to understand the water quality at the site over time; interconnections between aquifers or poor well completions may cause variations in chemistry and may indicate that shallow fresh water aquifers are being impacted by withdrawals.

EVALUATE RESERVOIR MANAGEMENT/BRINE TREATMENT OPTIONS

The team proposes the development of a well field for geologic carbon dioxide storage that combines CO_2 injection with brine extraction and where individual *dual-mode* wells are initially used to extract formation brine and subsequently used to inject CO_2. The wells will also be used to monitor the subsurface during pre-injection brine production so that key data

is acquired and analyzed prior to CO_2 injection. These data can be used to determine reservoir properties and to help guide reservoir operators in making follow-on well placement and flow-rate decisions. Overall, this pre-injection information can help achieve optimum subsurface CO_2 storage utilization. The extracted formation brine will be desalinated and treated for use in industrial applications including cooling tower makeup water and high purity water for steam.

Reservoir Management

This reservoir management approach addresses key needs for effective CO_2 storage. The first need is to cost-effectively acquire the data necessary to inform reservoir management decisions in a timely manner. Establishing that a site is potentially suitable for CO_2 storage—including minimizing the risk of CO_2 leakage—requires that sufficient data and information be acquired and analyzed prior to CO_2 injection. Site suitability requires identifying a caprock with sufficient seal integrity for containing the buoyant, pressurized CO_2 plume. A sufficiently tight caprock seal is also necessary to efficiently reduce pore pressure by extracting brine. Site suitability also requires that the target CO_2 storage zone(s) have sufficient compartment volume(s) for the intended CO_2 storage capacity without incurring too much pore overpressure (defined to be pore pressure above ambient). CO_2 storage capacity may be greatly increased with a reservoir pressure management strategy that extracts brine from the CO_2 storage compartment. Such a strategy may also mitigate various operational and environmental risks.

Reservoir pressure management using separate CO_2-injection wells and brine-extraction wells has been considered in many CO_2 reservoir studies (Bergmo et al., 2011; Birkholzer et al., 2012; Breunig et al., 2013; Buscheck et al., 2011, 2012; Court et al., 2012; Dempsey et al., 2014; Heath et al., 2013; 2014; Hermanrud et al., 2013; Roach et al., 2104). The trade-off between achieving early pressure relief and delayed CO_2 breakthrough has been identified as a key operational challenge. Early pressure relief requires close well spacing between the CO_2 injectors and brine producers, but delayed CO_2 breakthrough requires large well spacing (Buscheck et al., 2012). The use of separate injectors and producers requires good hydraulic communication between those wells, which cannot always be guaranteed. Many geologic formations are compartmentalized (Hansen et al., 2013; Shi et al., 2013), which can limit hydraulic communication between wells and reduce the direct benefit of extracting brine to relieve pressure at the CO_2 injection well. Early CO_2 breakthrough may require that brine extraction at the affected wells be abandoned and additional brine-extraction wells be installed elsewhere. Overall, early CO_2 breakthrough and poor hydraulic communication between wells can increase capital and operating costs of reservoir management. Accordingly, cost-efficient well-field operations, including cost-efficiency on a per well basis and cost-efficiency on a per mass of extracted brine basis, are key needs that can be addressed by effective reservoir pressure management.

The proposed approach (Buscheck et al., 2014) requires a shallow monitoring well and a minimum of two deep dual-mode brine-extraction/CO_2-injection wells completed in the candidate CO_2 storage target zones (Figure 20a). Initially, this will involve extracting brine from several candidate CO_2 storage target zones, while monitoring the pressure response in an adjoining deep monitoring well and in a shallow monitoring well (Figure 20a). The goal is to identify a CO_2 storage target zone that is overlain with a caprock seal that is sufficiently tight to constrain the upward migration of buoyant CO_2 and to prevent the downward migration of brine during the pre-injection brine-extraction stage (Figure 20a). Preventing this downward brine migration is important because any downward flux of brine into the target CO_2 storage zone would partially defeat the purpose of brine extraction—to reduce pore pressure, and thus accommodate more CO_2 injection without incurring too much pore overpressure. Once a suitable CO_2 storage target zone is identified, additional brine extraction can continue in that zone until the pressure perturbation is sufficient to inform reservoir managers about the hydrologic properties of the CO_2 storage reservoir. Together with the pressure response at the shallow monitoring well, this extended pressure drawdown test (Figure 21) can be used to estimate the effective compartment volume of the target CO_2 storage zone and the contribution of caprock leakage on pressure relief.

During the pre-injection brine-extraction stage, an ensemble of tracer slugs can be released along the second deep dual-mode well (the deep monitoring well in Figure 20a). Tracking the arrival times of the respective tracer slugs at the brine-extraction well can help forecast the CO_2 breakthrough time that will occur during the CO_2 injection stage (Figure 20c). Together with pressure measurements (Figure 21), this information can help reservoir managers plan the timing and rates of CO_2 injection and brine extraction that will be implemented during the CO_2 injection stage (Figures 20b and 20c).

Monitoring pressure and the migration of the CO_2 plume during the CO_2 injection stage will provide useful information that may be used to locate a *potential* third dual-mode well that could be used for brine extraction (if the decision is made

to extend CO_2 storage operations). This process would involve moving CO_2 injection from the first to the second dual-mode well (Figure 20d).

A key advantage of the proposed approach is that CO_2 is injected at the location of maximum pressure drawdown due to the pre-injection brine extraction. Thus, it will take some time before pore pressures in the vicinity of the dual-mode CO_2-injection well reach initial formation pressure prior to brine extraction. Consequently, pre-injection pressure drawdown *buys time* and allows reservoir operators to locate the next dual-mode brine-extraction well further away from the CO_2 injector than would be possible if separate *single-mode* CO_2 injectors and brine producers been used. This increased well spacing will delay CO_2 breakthrough and extend the operating lifetime of the dual-mode brine-extraction well. Altogether, this approach greatly reduces the total number of wells required to execute reservoir pressure management, which will result in reduced capital cost. Because this approach requires less brine extraction to achieve a targeted level of pressure relief than would be required with separate single-mode CO_2 injectors and brine producers, this approach also reduces operating cost.

In summary, the proposed approach is designed to provide timely, cost-effective information and pressure reduction where it is most needed: at the center of the CO_2 storage zone. Moreover, this approach can identify the target CO_2 storage zone that will be most suitable for CO_2 injection, prior to that injection. This understanding reduces environmental and financial risk. The dual-mode well approach can achieve reservoir pressure management with fewer wells and with less brine extraction than an approach that uses separate single-mode wells, which will reduce capital and operating costs. This approach also generates product water earlier, which accelerates the utilization benefits.

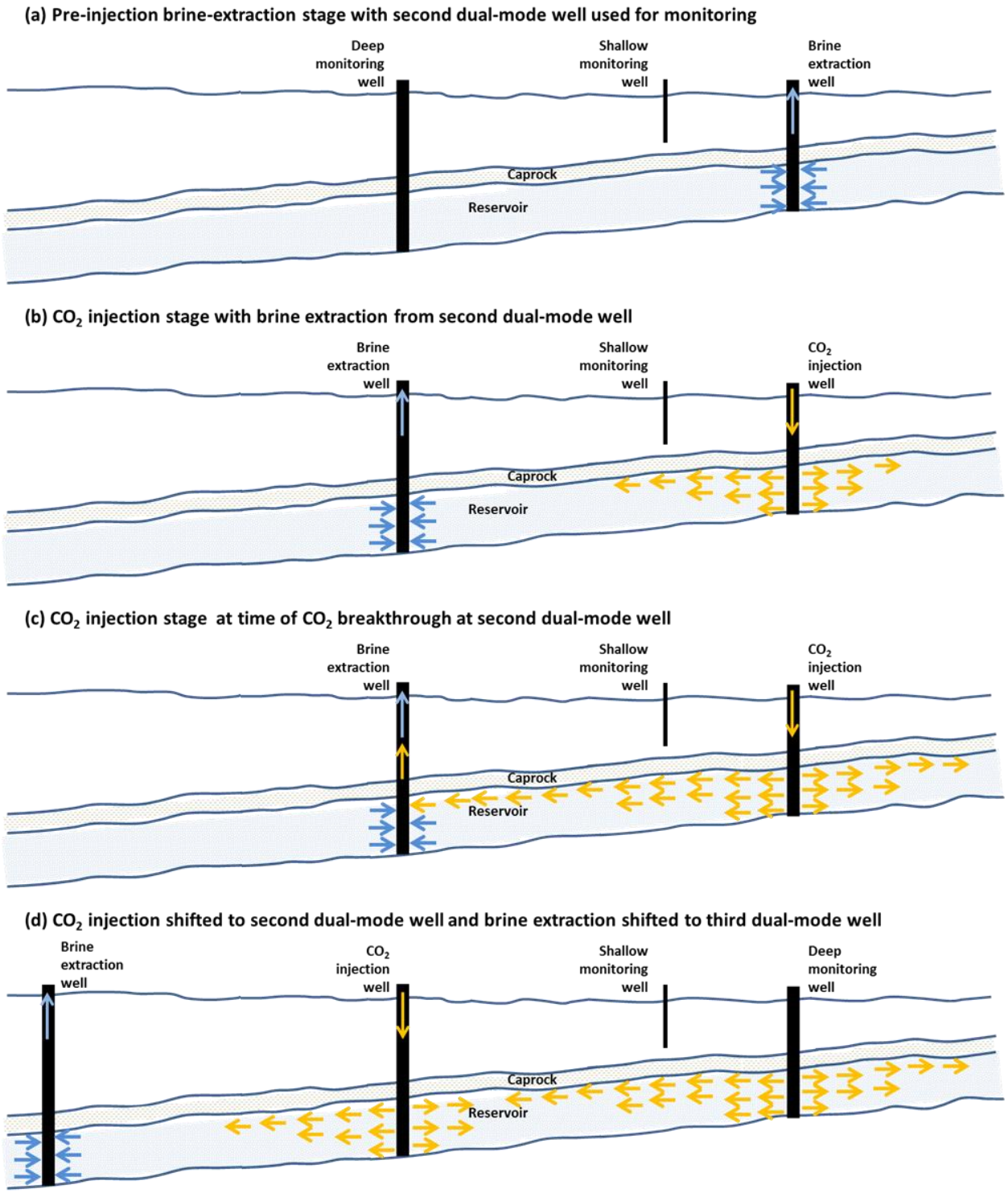


Figure 20: Reservoir pressure management using *dual-mode* brine-extraction/CO_2-injection wells during (a) pre-injection brine-extraction stage, (b) CO_2 injection stage, with concurrent brine-extraction from the second dual-mode well, (c) CO_2 injection stage at the time of CO_2 breakthrough, and (d) optional CO_2 injection stage, with CO_2 injection shifted to the second dual-mode well and brine extraction shifted to added (third) dual-mode well. A shallow monitoring well completed above the caprock is used to monitor pressure and assess seal integrity. The second and third dual-mode wells should be completed down-dip of the first dual-mode well to take advantage of gravity segregation, to delay CO_2 breakthrough.

Proposed Task Timeline for Reservoir Management

1) Drill and complete two deep dual-mode wells into proposed storage aquifer(s) with an additional shallow monitoring well completed above cap-rock (Figure 20). To provide operational flexibility, each well should be capable of functioning as a:

CO_2 injection well:

- Selective injection of CO_2 into specific target zones

Brine production well:

- Selective extraction of brine from specific target zones

Monitoring well:

- Full monitoring instrumentation to acquire temperature, pressure, fluid samples, and CO_2 detection (suggest using technology and methods developed by LBNL and others in support of SECARB)
- Monitoring wells must be able to determine pressure perturbations caused by brine removal and be able to detect the breakthrough of CO_2 and aqueous-phase tracers

2) Begin producing brine from brine extraction well (Figure 20a)
   a. Recommended rate of removal and total mass of brine to be removed will be determined by modeling calculations to be carried out in follow-on feasibility study.
3) Monitor pressure perturbations in monitoring well(s)
   a. Use data to determine cap-rock seal integrity
   b. Estimate CO_2 breakthrough travel time into deep monitoring well
4) Stop extracting brine and begin injecting CO_2 at the first dual-mode well (Figure 1b)
5) Begin extracting brine (Figure 20b) from second dual-mode well, which was the deep monitoring well during the pre-injection stage (Figure 20a). The transition time will be determined from modeling carried out in feasibility study.
6) Continue brine extraction and CO_2 injection until CO_2 breakthrough occurs in brine extraction well (Figure 20c).
7) Stop injection/extraction operations or, if project continues, repurpose the brine-extraction well into a CO_2 injection well and drill a new dual-mode well with which to continue brine extraction (Figure 20d). The location of third dual-mode well will be determined using data on reservoir properties acquired during the pre-injection and injection stages of testing.
8) Continue to expand the well field as needed (Figure 20d).

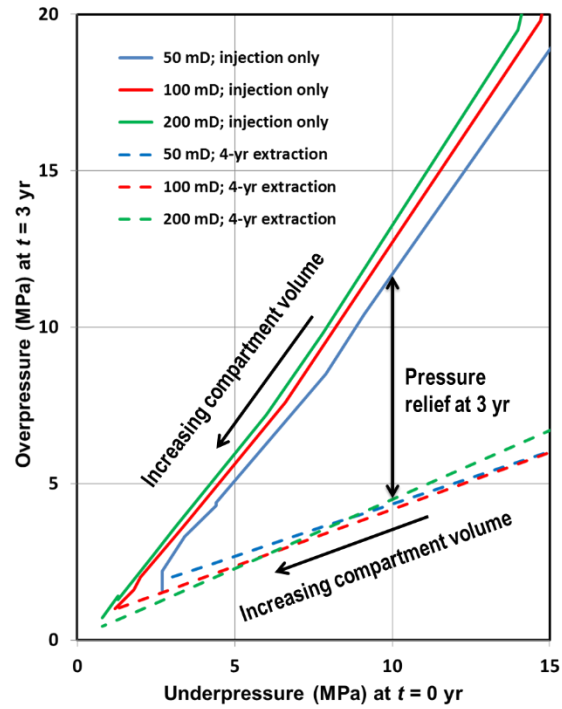


Figure 21: Overpressure three years into CO_2 injection stage is plotted as a function of underpressure after 4 years of pre-injection brine extraction (dashed lines). Also plotted is overpressure for the corresponding cases with no brine extraction (solid lines). Reservoir permeability values of 50, 100, and 200 mD are considered. Caprock permeability is 0.001 mD. A wide range of reservoir compartment area (1 to 300 km^2) and thickness (100 to 300 m) are considered. CO_2 injection rate and brine extraction rate is 1 million tonnes/year, which is greater than the rate planned for the pilot test. The one-to-one correspondence between underpressure and overpressure directly informs reservoir operators about the CO_2 storage capacity as a function of brine extraction rate, including the case of no brine extraction (Buscheck et al., 2014).

Water Treatment

Water treatment will begin when brine extraction begins. For the estimated rate of carbon dioxide injection of 100,000 tonnes per year, assuming a one-for-one volume replacement, and a carbon dioxide density in the subsurface of 0.8 kg/m^3, approximately 125,000 m^3/year of brine needs to be extracted. This corresponds to a production rate of 4 L/s (63 GPM). Membrane-based desalination equipment for this feed flux is generally available as portable skid-mounted units at costs in the range of USD150,000-250,000 depending on the extent and types of pre-treatment needed. Additional equipment will be needed for further treatment to produce ultrapure water such as for boiler water makeup. Total costs of water treatment are therefore likely to be less than USD500,000 for the fairly low salinity and benign fluid compositions expected for the site.

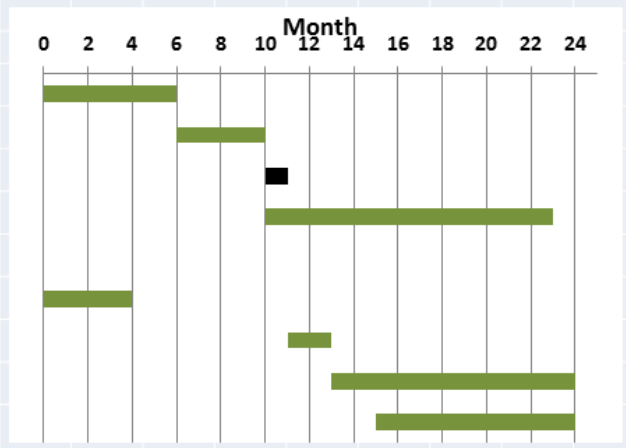
Although it would be desirable to delay the design and procurement of the water treatment pilot plant until actual brine samples are obtained from the well, the team recommends to go ahead with design and procurement at the beginning of the project. The design will be based on available water quality data obtained from wells in the vicinity of the proposed carbon dioxide capture site. Design of the plant configuration is highly dependent upon salinity, and the selection of pre-treatment steps depends on the details of the fluid compositions. However, given the fairly low salinity of the waters

sampled from wells in the vicinity of the site, the team will start with a reasonable upper limit on fluid salinity and specify a treatment system that can be modified to treat fluids at that or lower salinities. The team believes that the additional cost for that versatility offsets the delay in project timing that would arise if the equipment order is delayed until actual brines are available.

Salinities of formation waters in the vicinity (Gangzhong-Liujianfang area) range from about 3000 to 11,000 mg/L TDS. These waters are much less saline than seawater (36,000 TDS) and are very treatable using commercially available membrane-based systems. The compositions are also fairly benign in terms of hardness and scaling potential. There are a few fluids of higher salinity that have been found, for example waters as high as 49,520 ppm TDS in the Middle-eastern part of North Danang. If such fluids are produced from the wells, the team would have to either reduce the feed flux or acquire additional equipment to maintain the planned rate of water treatment. One potential problem may arise if large amounts of organic compounds—which are known to foul reverse osmosis membranes—are present. Additional pre-treatment steps may be needed if this is the case. Such equipment can be added to an existing treatment system at some amount of additional cost.

Project timeline (Times are rough estimates to be refined with reservoir simulations carried out as part of feasibility study):

Tasks		Start	Duration	Finish
Reservoir Management	1			
Well drilling and completion	1.1	0	6	6
Brine extraction	1.2	6	4	10
Obtain representative brine sample	1.3	10	1	11
CO2 injection/brine extraction	1.4	10	13	23
Brine Management	2.0			
Brine treatment specifications	2.1	0	4	4
Procure brine treatment equipment	2.2	11	2	13
Treat brines	2.3	13	11	24
Evaluate treated fluids for industrial uses	2.4	15	9	24



MAJOR OUTCOMES AND FINDINGS

The team addressed the following seven key questions:

1) In a broad sense, is the EWR concept technically feasible?

   Yes, suitable target formations (Guantao and Dongying) are available near the GreenGen facility, the formation water is only mildly saline. So, storage capacity exists and treatment of withdrawn water for use in the power plant and other applications is realistic.

2) Reservoir properties-suitable/non suitable

   Yes, two potential reservoir formations were identified: the Guantao and Dongying. Both have excellent porosity and permeability and contain water that would be conducive to treatment for industrial and agriculture uses. The team recommends using the Guantao formation as it is shallower-1500 m, and contains water of lower salinity than the Dongying. These factors will reduce EWR expense and yield greater useable water volumes.

3) Reservoir storage (caprock) integrity

   While further, detailed investigation is needed, it appears that the Minghuazhen shale/mudstone unit overlying both the Guantao and Dongying formations would serve as a suitable caprock.

4) Does the team have a legitimate Injection/withdrawal strategy?

   Yes, the team proposes using dual mode wells that will serve as both CO_2 injectors and brine producers. First, brine will be withdrawn, then CO_2 will be injected into the resulting void space. As CO_2 dissipates, the cycle will be repeated until the capacity of the well is reached. Additional wells can then be developed for the next injection stage. This strategy yields maximum control over the distribution of CO_2 in the formation while minimizing the number of wells that will be needed, thus lowering capital costs.

5) Cost estimates-water treatment

Treatment of withdrawn formation water to meet either boiler feed or cooling water standards are estimated to result in recovery rates between 92% and 95%. Treatment costs will be sensitive to the presence of organic compounds in the formation water. Estimated average operating costs for treatment of Guantao formation water to meet power plant boiler feed or cooling water needs would range between USD 2.37 and USD 2.92/m^3 (RMB 14.59-17.97/m^3). Treatment to remove organic compounds would add about USD 1.50 to the water treatment cost. These costs reflect a small scale reverse osmosis (RO) treatment unit treating 400 m^3/day. Capital costs for a 400 m^3/day RO unit would be about USD 500,000. Economies of scale would result in lower unit costs for a larger RO system.

6) Cost estimates-reservoir management

At the pilot scale, the costs for CO_2 injection and water withdrawal would involve two dual mode wells completed in the Guantao formation and one shallow observation well. To minimize capital expenditures during the pilot phase, trucking of compressed CO_2 and extracted formation water is recommended.

7) Recommend/do not recommend proceeding to Phase 2

The team recommends proceeding with the Phase 2 study. It will clarify, at reasonable capital and operating costs, the practical considerations of using captured CO_2 to drive water recovery and provide a strategy for making power generation either neutral or net positive with respect to water balance. In particular, the study will identify key parameters that need to be defined prior to considering CCUS/EWR and it will provide a protocol for evaluating the costs and performance of large scale operations prior to implementation.

Longer term implications of Phase I work:

1) Formation management for CCUS/EWR has not been done before in conjunction with an operating power plant, so should this project go forward, there will be a wealth of operating data that will be useful to power plant owner/operators that do not have an EOR option;
2) Formation management offers the hope that aquifer pressures can be moderated thus reducing the risk of a "catastrophic" leak. With operating data in support of this, the ability to obtain the injection permit should ease. A second benefit would be the ability of the formation to store larger volumes of CO_2. Both these benefits should reduce storage costs.
3) This project initiates a series of studies which, culminating in a full scale demonstration would develop tools needed to identify suitable geologic formations for CCUS/EWR, develop realistic CO_2 injection and water withdrawal strategies and while evaluating cost and performance estimates.

Conclusions

As part of a prefeasibility study, the team has generated detailed reports on many aspects of a proposed enhanced water recovery (EWR) scheme tied to the GreenGen IGCC power plant in Tianjin PRC. EWR uses CO_2 injection to maintain pore pressure near initial conditions during groundwater withdrawals, reducing the risk of induced seismicity, CO_2 leakage, and subsidence.

These reports include reviews of available geologic data and groundwater chemistry data, a review of novel injection strategies to reduce the number of wells needed to better utilize the storage potential of the injection reservoir, and a review of potential water treatment strategies. Further, two reports used the review data to generate 1) preliminary analysis of water treatment costs and 2) the performance of the reservoir under a simple injection scenario.

From these reports, the team has compiled a list of recommendations to pursue during a more detailed Phase 2 feasibility study of the project. The goal of the Phase 2 feasibility study is to gather enough data to refine calculations initiated in the prefeasibility study. Once Phase 2 is completed, the project should be ready to begin an engineering analysis to develop a functioning pilot project.

Collection of sufficient data will require tight collaboration and data sharing with energy companies (oil/gas/geothermal). If such collaboration is not possible, project costs will likely be quite high as new 3-D seismic, test wells, and geologic interpretation will have to be performed. Additionally, the composition of the CO2 stream will need to be introduced into our calculations for a true feasibility study. Perhaps the most important of these are the quality and quantity of the injected CO_2 gas stream. Finally, in-country costs will need to be compiled for the analysis to be truly relevant to China.

Forming a team of industrial/economic researchers in China is recommended to determine costs for all aspects of the project that can be used for project cost calculations in Phase 2.

RECOMMENDATIONS FOR PHASE 2

Recommendations are split into five primary categories.

1) Geologic Data: A primary recommendation for Phase 2 will be to gain access to more detailed site specific geologic data. This likely could be from existing wells and 3-D seismic surveys. The fault bounded reservoir block chosen as an example for the prefeasibility study appears to be a good candidate for EWR, however other blocks within a reasonable radius from GreenGen should be examined in Phase 2. Existing data from oil/gas/geothermal exploration should be brought together to allow such an analysis. Once an injection target is chosen, data from boreholes within the target block should be gathered. Of particular interest will be the overpressure with depth, thickness and permeability of sand layers, fracture gradient, and in-situ stress field. If no borehole data can be found, it will be necessary to drill at least one new borehole to ground truth 3-D seismic density inversions, determine the local stress state, and to provide formation scale pump test data on permeability and specific storage. 3-D seismic density maps of the target formations will allow high resolution analysis of likely injectivity and plume migration behavior. Such detailed analysis will reduce project risk and increase the likelihood of success. Measurement of the local stress state will be necessary to better predict the likelihood of induced seismicity. Storage capacity generated from such high resolution 3-D numerical simulations will likely be more realistic than current rough estimates based on homogeneous layered permeability. Pump test data between 2 wells would be ideal for estimating reservoir connectivity at the scale of the expected CO_2 plumes (1-2 km radius). Multiple screens in each of the highly conductive layers would allow cross well tests between conductive layers to determine pressure connections between layers. Pressure transducers at the top of the proposed regional seal (Minghuazhen Formation) could be used to confirm this assumption. The pump tests could be undertaken as part of the pilot test as described by Bourcier and Buscheck (LLNL) in the prefeasibility analysis, however some pump testing before full commitment to a pilot test may be preferable from a risk standpoint.
2) Groundwater Quality Data: Site-specific ground-water quality data will be required to allow more accurate assessment of treatment needs. During Phase 2, analysis should include full chemistry suites capturing any hydrocarbon constituents, trace elements, pH, and temperature in addition to the typical bulk chemistry data (TDS, Ca, Na, K, Cl, B, etc.), particularly constituents that can for mineral scale in treatment systems. The data collection will allow calculation of saturation index of potential scale forming compounds (e.g., $CaCO_3$) that may cause fouling problems for water treatment system and IGCC boiler operation. Data should also be collected during well drilling and pump testing to determine the range of possible water quality scenarios and to measure the potential for interconnection between the target formation and overlying formation waters. Of particular importance for this are indicators of surface contamination, such as nitrate, and stable isotopes to bracket water ages and sources. Shallow ground-water monitoring wells may be needed to verify that migration from shallow aquifers is not occurring; either within test wells (cross-contamination) or via vertical migration (e.g., fractures).
3) Quality and quantity of the captured CO_2 stream: This category includes information on exhaust pressure, exhaust composition (N_2, SO_4, H_2S, CO_2, water vapor, etc.), ease of building pipeline from the plant to the injection location, and boiler water requirements (for treated groundwater). Exhaust pressure is very important for calculating compressor design because even 50psi above atmospheric pressure can reduce the required compressor stages from 5 to 4. Subsurface injection can remove H_2S and SO_4 from the effluent stream, reducing costs for cleaning at the plant. Logistics of pipeline construction will be vital to a long term project with injection mass of 1 MT/yr. The simple assumption of truck transport for CO_2 for the 0.1 MT/yr case is not realistic for 10x more CO_2 injection.
4) Water Treatment Design: Expand the prefeasibility analysis to include costs of plant construction, energy credit for heating, treatment processes other than membrane systems, and site-specific chemistry data. The team will need to find real numbers for water treatment needed for IGCC boiler operation (maximum SiO_2, B, etc. for the actual GreenGen boiler). Further work will need to be done to better understand the site configuration, transportation distances, and disposal options and costs for a site-scale evaluation. It is critical to understand the water quality at the site over time; interconnections between aquifers or poor well completions may cause variations in chemistry and may indicate that shallow fresh water aquifers are being impacted by withdrawals. The regulatory framework that will define various steps such as disposal of brine concentrate, use of treated water, and hazardous constituents of concern also needs to be clearly defined.

5) Subsurface Risk Analysis: During Phase 2 it is recommended to develop a subsurface risk analysis for the project including risks from A) groundwater contamination, B) subsidence, C) induced seismicity, D) uncertainty in plume migration (lateral and vertical), E) CO_2 leakage above the caprock (through faults, wellbores, and caprock), F) uncertainty in injectivity, and G) uncertainty in reservoir capacity. As data gathered during Phase 2 become available, subsurface risks can be addressed using a variety of tools. One primary tool for risk analysis that the team has great familiarity with is CO_2-PENS, developed as part of the US National Risk Assessment Partnership (NRAP). CO_2-PENS was used in the GreenGen EWR prefeasibility study to address uncertainty in injectivity and plume radius with highly simplified assumptions; however, during Phase 2, this tool can be populated with much more complex data including 3-D reservoir models, site specific fault data, and locations of existing boreholes in the study area. Another tool that should be used for the Phase 2 risk analysis is a reservoir scale coupled stress/flow simulator to predict induced seismicity and subsidence due to perturbations caused by fluid injection and production. Finally, the project may want to explore the use of expert elicitation techniques used as part of several US Regional CO_2 Storage Partnerships. The quality of the risk analysis will depend largely on the quality of data that can be collected in support of Phase 2. The following references are included to support risk analysis concepts and include hyperlinks to the documents:

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CO_2 Algae BioFixation and Use

Joint Project

U.S. Research Team Lead

- University of Kentucky Center for Applied Energy Research, Department of Chemistry

U.S. Partners

- Duke Energy

China Research Team Lead

- Zhejiang University

China Partners

- ENN

Overview

In this theme, Chinese and U.S. researchers collaboratively conducted activities to improve understanding of the benefits of algae-based CO_2 capture and utilization from industrial point source emitters. Microalgae biologically fix 1.76 tons of CO_2 for every ton of biomass produced through photosynthesis. In principle the resulting biomass, which contains protein, carbohydrates and lipids as the main constituents, can be processed to produce a variety of products, thereby generating a revenue stream to offset the costs associated with carbon capture. Efforts focused on the identification of promising summer and winter algae strains for this application, the development and optimization of low-cost culturing systems, pilot-scale demonstration of the technology at a coal-fired power plant, and identification and evaluation of algae-derived products. The resulting data were used to construct a techno-economic model to estimate the overall cost of CO_2 capture.

Research Objectives

The objectives of this project were to develop and demonstrate an economically feasible technology for CO_2 capture and utilization using microalgae. During the course of the project efforts were focused on:

- The identification and culturing of optimal summer and winter algae strains to be used in the CO_2 mitigation system.
- Optimization of the culturing process and technology; this included the development of a low-cost photobioreactor (PBR) and demonstration of PBR-based algae cultivation at pilot-plant scale under summer and winter conditions, incorporating optimized nutrient and water recycling.
- Identification and evaluation of the possible co-products from the process, including fuels and animal feed.
- Use of the acquired data to construct a techno-economic model to estimate the overall cost of CO_2 fixation and utilization at various scales of operation.
- Development of a framework for collaboration between academic and industrial partners in both China and the U.S., leveraging each partner's specific aptitudes.

Summary of Research Activities

SUMMARY OF TASKS

Screening of Algae Strains

- *Scenedesmus acutus* was identified as a robust, fast growing production strain for CO_2 utilization from coal flue gas. The effects of pH, temperature, nutrient source, and water source were studied to optimize the growth (and thereby the CO_2 consumption) of this strain. Additionally, the produced biomass was analyzed to determine its elemental composition and the relative percentages of lipid, protein, and carbohydrates to better understand its utilization potential. From this effort, a fractionation approach was developed to produce both biofuels (from the lipid component) and bioplastics (from the defatted algae).
- Isolation and characterization of an invasive red alga species named *Coelestrella Sapiensis* from the photobioreactor at the East Bend Demonstration site was performed. This strain is a promising candidate because it grows readily in our standard growth conditions using industrial flue gas and from a utilization perspective its ability to turn red when stressed – indicating a potential to produce high value chemicals (such as pigments) – is promising.

Growth System Optimization

- Multiple vertical closed-loop PBRs were designed and prototyped. Different flow strategies (gravity fed vs. pressure driven) and orientations (parallel vs. series flow) were evaluated across multiple growth campaigns.
- In 2012 a pilot-scale PBR was constructed at Duke Energy's East Bend Station, a 650 MW coal-fired power plant. The PBR was seeded in December and a short winter growth campaign completed (Figure 1). In 2013 the PBR was expanded to a total system volume of 18,000 L and operated for a period of *ca*. six months.
- Based on the lessons learned in the foregoing activities, a radically different 'cyclic flow' reactor design was prototyped, tested and ultimately deployed at East Bend Station. This new reactor configuration promised more efficient use of sunlight and lower capital cost. Figure 2 shows the new reactor operating at East Bend Station during the summer of 2014.
- The cyclic flow PBR was refined during the winter of 2014-15 based upon lessons learned in the field and was re-deployed at East Bend Station during April 2015. During 2015, the reactor was operated continuously for 5 months, utilizing both coal flue gas and a mixture of bottled CO_2 and compressed air when flue gas was unavailable. The new reactor configuration enabled more stable operation, such that the system was able to produce more algal biomass in one growing season then had previously been grown over the course of the entire project.

Figure 43: Seeded 'serpentine flow' photobioreactor at East Bend (December 2012).

Algae Processing

- A low-cost/low-energy two stage dewatering process was developed. A low dose (3-5 ppm) of high molecular weight polyacrylamide cationic flocculent is used to aggregate the algae cells and induce settling. Clarified water is then recycled back to the system via a UV sterilizer (to control contamination) while the concentrated slurry is further dewatered via gravity filtration.

Figure 44: Rendering of cyclic flow reactor and picture of installed PBR (summer of 2014)

- Purified algal oil, extracted from *Scenedesmus* sp. harvested from the East Bend facility, was subjected to upgrading via catalytic decarbonylation/decarboxylation. This is a promising strategy for biofuel processing due to the relatively low levels of hydrogen and modest temperatures required. A low cost nickel based catalyst (developed at UK Center for Applied Energy Research (CAER)) was used to upgrade the crude algae oil to diesel range alkanes (Figure 7.3), demonstrating conversion of flue gas CO_2 to fungible hydrocarbon fuels.

Techno-economic Analysis

- A techno-economic analysis was performed to identify the major cost inputs to the system. The capital cost and installation of the algae growth facility was found to constitute over 90% of the overall cost of CO_2 capture. Hence, decreasing the cost of the installation is the best strategy to achieve an improvement in the economics. This realization led to the development of the next generation 'cyclic flow' reactor which incorporates cost savings derived from optimized tube spacing (to make more efficient use of capital) and a lower cost support frame.
- A life cycle assessment, based on 30% CO_2 capture from a hypothetical 1 MW coal-fired power plant, was performed for the new 'cyclic flow' PBR system to understand its impact on carbon dioxide emissions over its lifetime. The system was found to be CO_2 negative over its lifespan of operation, the two biggest contributors to CO_2 emissions being the acquisition and recycling of the PBR's tubes and the energy required to compress the flue gas for injection into the PBR.

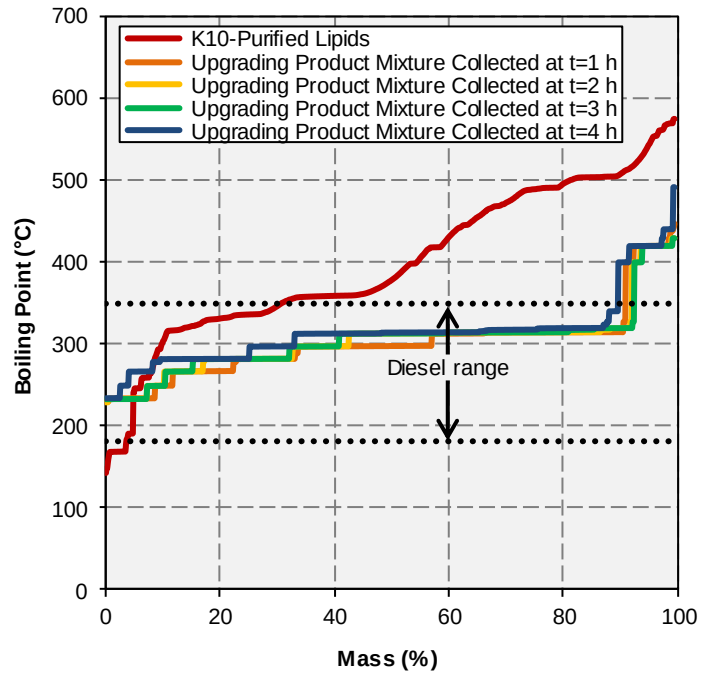

Figure 45: Simulated-distillation boiling point distribution plots of algal lipid feed ("K-10 Purified Lipids) and liquid product sampled at 1, 2, 3, and 4 h during decarboxylation/decarbonylation.

MAJOR FINDINGS AND OUTCOMES

- Multiple microalgae strains were evaluated for their suitability for CO_2 capture from flue gas, several promising strains being identified.
- One of the strains identified, *Scenedesmus acutus*, was found to exhibit strong growth using flue gas as the CO_2 source, while also reducing SO_2 and NOx emissions.
- An innovative photobioreactor was developed and tested, showing a significant reduction in required operating energy compared to its predecessor, in addition to lower capital cost and improved productivity.
- Various biomass utilization pathways were evaluated, informing the development of a fractionation approach to algal biomass valorization capable of producing multiple product streams to maximize revenue.
- A techno-economic model was constructed to better understand the economics of algae-based carbon capture and provide feedback to guide process improvements.
- A life cycle analysis of the algae cultivation system showed that the two biggest contributors to CO_2 emissions were the acquisition and recycling of the PBR tubes and the energy required to compress the flue gas for injection into the photobioreactor. The latest PBR design was confirmed to exhibit significantly lower energy consumption (and hence correspondingly lower CO_2 emissions) than its predecessor.

Major Achievements

China Patent Applications

- M. Wilson, J. Groppo, T. Grubbs, C. Cecil, M. Crocker, T. Liu and X. Zhang," Cyclic Flow Photo bioreactor System", China Patent Application No. 201510284884.2, May 28, 2015.
- M. Wilson, J. Groppo, T. Grubbs, C. Cecil, M. Crocker, T. Liu and X. Zhang," Cyclic Flow Photo bioreactor System – continuation application with other claims" (China Patent Application No. 201520355131.1, May 28, 2015).
- M. Wilson, S. Morton, J. Groppo, M. Crocker, A. Placido, T. Liu and X. Zhang, "Serpentine Photo bioreactor System" (China Patent Application No. 201520051553.X, January 26, 2015).
- M. Wilson, S. Morton, J. Groppo, M. Crocker, A. Placido, T. Liu and X. Zhang, "Serpentine Photo bioreactor System-continuation application with other claims" (China Patent Application No. 201510036773.X, January 26, 2015).

Know-how show-how licenses to China 3rd Party (non-exclusive licenses)

- License for Photo bioreactor technology for microalgae cultivation issued by University of Kentucky Research Foundation to Lian Heng Hui Investment Co., Dahong Meng Road, Fengtai District, Beijing, P.R.C., June 2, 2014. License is non-exclusive for the technology and field of use and territory is limited to China only.

List of Publications

- M.H. Wilson, D.T. Mohler, J.G. Groppo, T. Grubbs, S. Kesner, E.M. Frazar, A. Shea, C. Crofcheck, M. Crocker, "Capture and Recycle of Industrial CO_2 Emissions using Microalgae", submitted to *Appl. Petrochem. Res.*
- E. Santillan-Jimenez, R. Pace, S. Marques, T. Morgan, C. McKelphin, J. Mobley, M. Crocker, "Extraction, characterization, purification and catalytic upgrading of algae lipids to fuel-like hydrocarbons", *Fuel*, 2016, http://dx.doi.org/10.1016/j.fuel.2016.04.079.
- X. E, C. Crofcheck, M. Crocker, "Application of recycled media and algae-based anaerobic digestate in *Scenedesmus* cultivation", *J. Renew. Sustain. Energy*, 8(1) (2016) 013116.
- E. Santillan-Jimenez, T. Morgan, M. Crocker, "Continuous catalytic deoxygenation of model and algal lipids to fuel-like hydrocarbons over Ni-Al layered double hydroxide", *Catal. Today*, 258 (2015) 284.
- M.H. Wilson, J. Groppo, A. Placido, S. Graham, S.A. Morton III, E. Santillan-Jimenez, A. Shea, M. Crocker, C. Crofcheck, R. Andrews, CO_2 recycling using microalgae for the production of fuels, *Appl. Petrochem. Res*. 4 (2014) 41.
- H.-Y. Shin, J.-H. Ryu, S.-Y. Bae, C. Crofcheck, M. Crocker, "Lipid extraction from Scenedesmus sp. microalgae for biodiesel production using hot compressed hexane", *Fuel*, 130 (2014) 66.
- A.E. Harman-Ware, T. Morgan, M. Wilson, M. Crocker, J. Zhang, K. Liu, J. Stork, S. Debolt, "Microalgae as a renewable fuel source: fast pyrolysis of Scenedesmus sp.", *Renewable Energy*, 60 (2013) 625.
- C. Crofcheck, X. E, A. Shea, M. Montross, M. Crocker, R. Andrews, "Influence of flue gas components on the growth rate of *Chlorella vulgaris* and *Scenedesmus acutus*", *Transactions of the ASABE*, 56(6) (2013) 1421.
- C. Crofcheck, X. E, A. Shea, M. Montross, M. Crocker, R. Andrews, "Influence of media composition on the growth rate of *Chlorella vulgaris* and *Scenedesmus acutus* utilized for CO_2 mitigation", *J. Biochem. Tech.*., 4(2) (2012) 589.

Commercialization

Commercialization efforts are already underway with a Chinese company (third party, not in CERC) to scale up the UK CAER photobioreactor technology to produce high value nutraceuticals and bioplastics. In support of this endeavor, 4 patent applications have been submitted and a licensing agreement has been signed. Further investment in R&D will be required to increase system productivity while decreasing capital and operating costs to fully realize the commercial potential of this technology.

Conclusions

Algae-based biotechnology has the potential to convert CO_2 emissions into a variety of products, enabling the monetization of carbon emissions. The CERC-ACTC has provided a strong framework for knowledge sharing between the U.S. and China, via both industry and academia. This program has catalyzed collaborations both inside and outside the CERC and provided important support to several developing technologies. UK CAER looks forward to continuing these fruitful relationships and making further progress during the next phase of the CERC.

Integrated Industrial Process Modeling and Additional Topics

Collaborative Project

U.S. Research Team Lead

- West Virginia University

U.S. Partners

- National Energy Technical Laboratory

China Research Team Lead

- Tsinghua University

China Partners

- Chinese Academy of Sciences
- China Electric Power Consulting Company
- Shenhua
- Huaneng

Overview

The major focus of the research from the U.S. side in Task 8 was the development of steady-state and dynamic models for a monoethanolamine (MEA)-based CO_2 capture process for a 550 MWe post-combustion, supercritical, pulverized coal (PC) plant. The steady-state model developed in Aspen Plus included the steam-side of the power plant integrated with the MEA-based capture system. The combined system was optimized to minimize the levelized cost of electricity (LCOE) for 90% carbon capture. Using this model, a dynamic model was developed and used to design controllers for both proportional-integral-derivative (PID), advanced linear and non-linear model predictive control (LMPC and NMPC), and robust control using Aspen Plus Dynamics. The controllability of the whole process was investigated over a wide range of operating conditions, including the simultaneous ramping up/down of the power with changing CO_2 target levels. It was found that the NMPC model was superior to PID and provided stable control. Other work comprised a study of using supercritical CO_2 as the working fluid in a Brayton power cycle and work improving an existing 3D immersive training system for an IGCC power plant.

Research Objectives

- Develop a steady state model to predict the behavior of post-combustion, carbon capture processes.
- Develop a dynamic model to predict the transient behavior of post-combustion, carbon capture processes.
- Reconcile the steady state and dynamic models if differences exist.
- Investigate and model (steady state and dynamic) the integration of carbon capture processes with the power plant through the use of steam in the absorber reboiler.
- Optimize the steady state model to give the lowest levelized cost of electricity.
- Evaluate the dynamic response of carbon capture processes in the light of load-following operations.
- Develop effective control strategies for load following operations and disturbance rejection.
- Upgrade the existing facilities 3D immersive training system for IGCC power plant.
- Investigate the use of supercritical CO_2, as opposed to steam, as a working fluid in a simple Brayton power cycle.

Summary of Research Activities

SUMMARY OF TASKS

Steady-State and Dynamic Modeling of Supercritical CO_2 Recompression Brayton Cycle

In this work, the complete process model of a 10 MW sCO_2 recompression Brayton cycle was developed in the MATLAB-Simulink environment to study both steady-state and dynamic performance. Two different dynamic simulations were performed including a 10% decrease in heat input with open-loop response and a 10% decrease in heat input with a PI controller for maintaining a constant sCO_2 cooler outlet temperature.

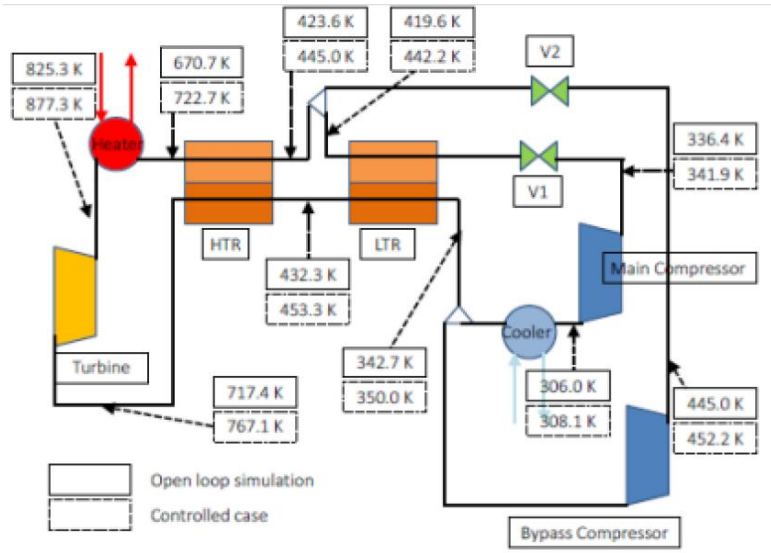

Figure 46: Final Steady-State Temperatures for the Open-Loop Controlled Cooler Temperature Case

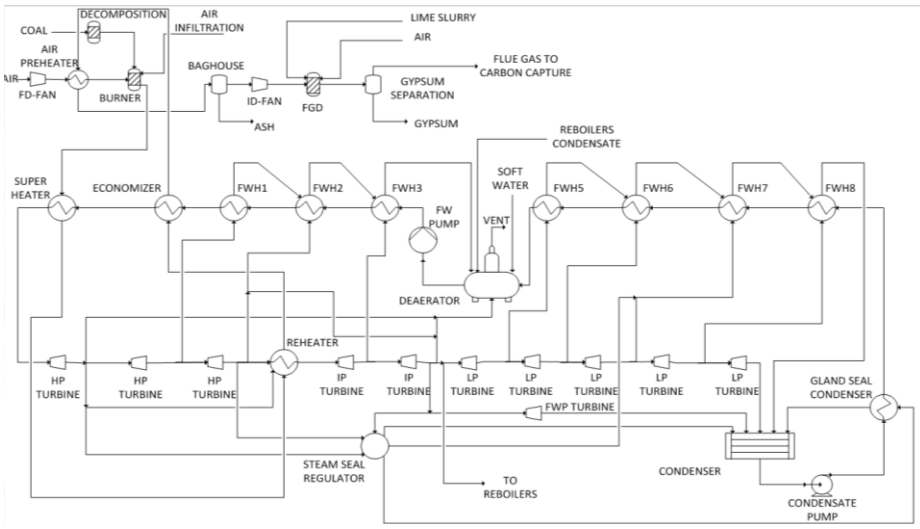

Figure 47: Flow Diagram of Steam-side of Super Critical Pulverized Coal Power Plant

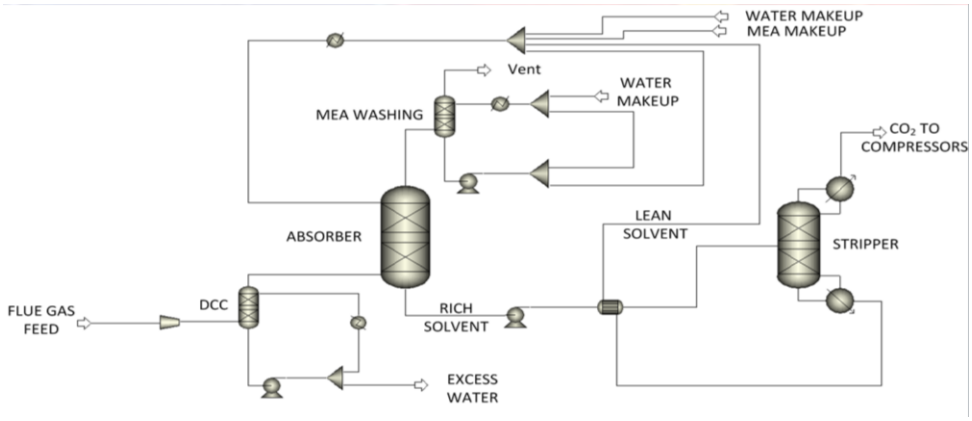

Figure 48: Flow Diagram of MEA-based Carbon Capture Process (integration between Figures 2 and 3 is through the steam take off marked as "To Reboilers" in Figure 2)

Table 6: Results of Optimization of Steady State Power Plant and integrated CO_2 Capture Process

net power without CO_2 capture (kW)	549,990
net plant efficiency without CO_2 capture (HHV)	39.30%
power loss due to flue gas blower (kW)	3,237
power loss due to CO_2 compressor (kW)	33,344
power loss due to rich solvent pump (kW)	178
power loss due to steam to reboilers (kW)	92,980
net power with CO_2 capture (kW)	420,251
net plant efficiency with CO_2 capture (HHV)	30.03%
efficiency penalty	9.27%
CO_2 capture	90%
heat duty per ton CO_2 recovered (GJ/ton)	3.07

Systems Modeling of Post-Combustion Capture Technology

The following activities in chronological order of implementation were:

- Developed a steady state model of an MEA-based CO_2 capture process integrated with the steam side of a supercritical pulverized coal power plant.
- Optimized the steady state model to minimize COE under the constraint of 90% CO_2 capture.
- Created a dynamic model of the integrated based CO_2 capture process with the normal operating point corresponding to the optimized case.
- Customized the dynamic model to include accurate models for the rate-based absorber/stripper units using a modified Murphree efficiency based on the flue gas flowrate, solvent loading, solvent flowrate, and CO_2 loading.
- Customized the dynamic model to include an accurate model for the prediction of pressure drop in the packed towers from low liquid loadings through the flooding regime.
- Developed a basic PID control structure for the control of the CO_2 capture process.
- Performed system identification on the dynamic model to determine a suitable linear model for the implementation of a linear model predictive control (LMPC) strategy.
- Compared the LMPC to PID control and demonstrated the superiority of LMPC over a wide range of operating conditions and disturbances.

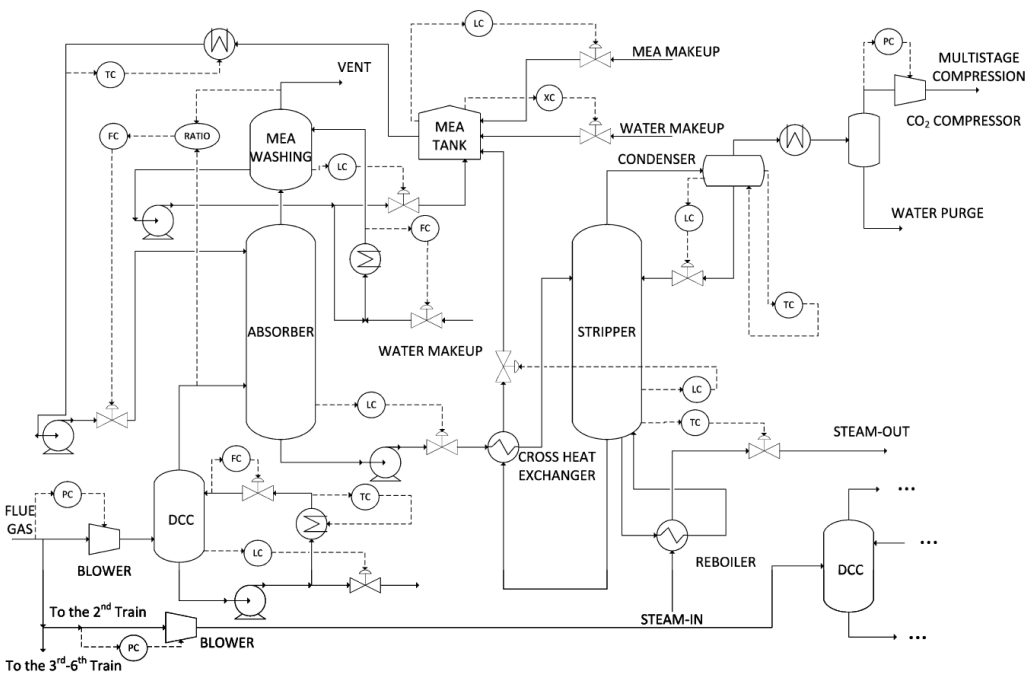

Figure 49: Plant-wide Control Structure for MEA-based CO_2 Capture Process

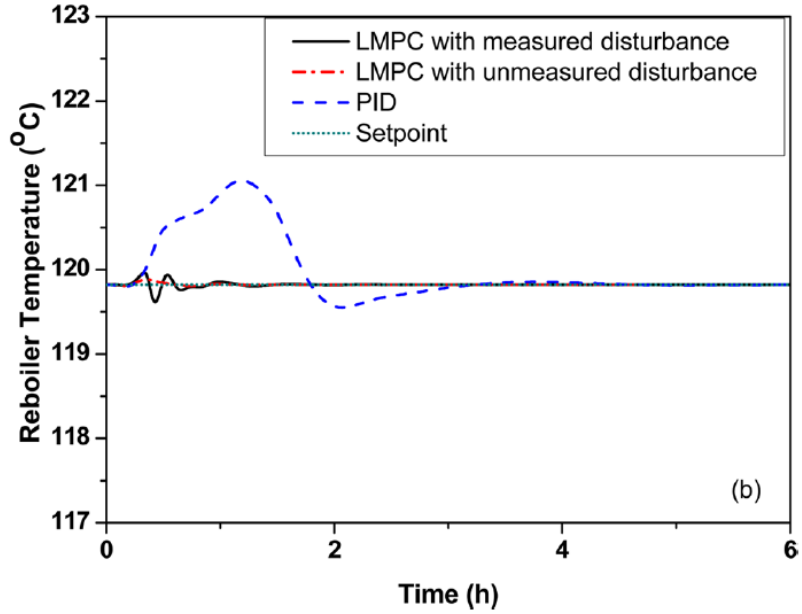

Figure 50: Performances of MPCs and PID due to 5% ramp decrease in flue gas flow rate and CO_2 composition of flue gas: (a) CO_2 capture rate control and (b) stripper reboiler temperature control.

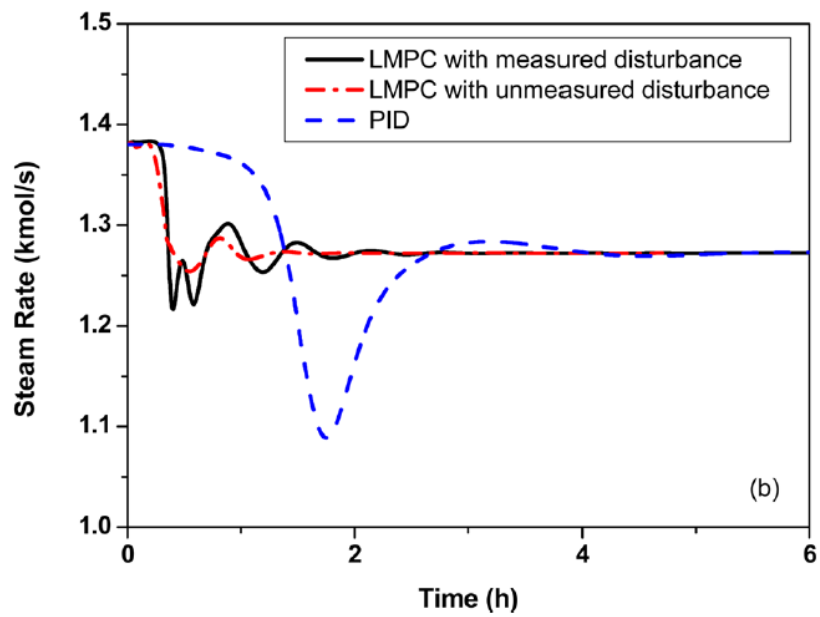

Figure 51: Transients of manipulated variables in response to 5% ramp decrease in flue gas flow rate and CO_2 composition of flue gas: (a) lean solvent flow rate and (b) low pressure steam rate.

- Developed a flooding control strategy.
- Developed a non-linear model predictive control strategy.
- Developed a robust control strategy.
- Testing (currently) each of the control strategies at different operating points and different combinations of disturbances.

Initialization of Dynamic Model with Immersive Visualization

- Initialization and augmentation of a dynamic model with immersive visualization capability for a generic IGCC system with gas turbine and steam bottoming cycle.
- WVU's operator training system (OTS) and 3D immersive training system (ITS) was upgraded in this task.

- Demonstration of the 3D system and OTS was demonstrated to the group from Tsinghua University during the 2013 CERC workshop, in Morgantown.

MAJOR FINDINGS AND OUTCOMES

The development of functional, realistic dynamic models of processes to be deployed in post-combustion CO_2 capture from existing coal-fired power plants is essential to understanding potential difficulties in operating such systems. Although, MEA-based, CO_2-capture technology is relatively mature, the scale at which it must be deployed for power plant operations presents additional challenges. The work developed in CERC Task 8 shows that advanced linear model predictive control (LMPC) techniques can be used to control emission levels and target CO_2 capture rates under a wide variety of turn-down scenarios. In addition, control strategies for multiple absorber-stripper systems deployed in parallel (to accommodate the massive volumetric flowrate of flue gas) have been developed that minimize CO_2 emissions in the case when flooding in one or more of the absorbers occurs due to increased flue gas flow.

Major Achievements

Workshops

- Participated (R. Turton and Q. Zhang) in US-CERC -Task 8 workshop held in Beijing at Tsinghua University May 27-28.
- Participated (R. Turton, D. Bhattacharyya, and Q. Zhang) in US-CERC -Task 8 workshop held in Morgantown, WV, October 7-8, 2013

List of Publications

- Qiang Zhang, Richard Turton, and Debangsu Bhattacharyya, *Development of Model and Model-Predictive Control of an MEA-Based Postcombustion CO_2 Capture Process*, Ind. Eng. Chem. Res., 55 (5), pp 1292–1308 (2016)
- Zhang Q, Bhattacharyya D, Turton R,, "Model Predictive Control of Post-Combustion CO_2 Capture Process Integrated with a Supercritical Pulverized Coal Plant", Paper 278h, AIChE Annual Meeting, Atlanta, GA, November 16-21, 2014
- Zhang Q, Bhattacharyya D, Turton R, "Dynamic Modeling and Control of Post-Combustion CO_2 Capture Process Integrated with Supercritical Pulverized Coal Plant", Paper 493e, AIChE Annual Meeting, San Francisco, CA, November 3-8, 2013
- Zhang, Q., Bhattacharyya D, Turton R, Dynamic modeling and control of post-combustion CO_2 capture process integrated with supercritical pulverized coal plant, 2013 International Pittsburgh Coal Conference, Beijing, CHINA, September 16-19, 2013

Collaboration

The team collaborated with Prof. Li's group from Tsinghua University over the course of the first phase of CERC. The team hosted joint workshops both at Tsinghua and WVU, Morgantown in which progress on a variety of projects were discussed. The groups at WVU and Tsinghua have considerable overlapping research interests and both groups are committed to continuing and expanding these collaborations. WVU's expertise in simulation using commercial software can help Tsinghua University's modeling efforts and Tsinghua University's knowledge of power plant systems (in China) and their access to data can significantly enhance WVU's modeling and verification efforts.

In the next phase of CERC, significant participation and collaboration with U.S. industry is expected. The work in the next phase of CERC will focus on the effects of cycling on existing coal-fired and natural gas fired power plants and strategies will be developed to determine how to deploy different power plants in an optimal way given a sequence of time varying power demand.

Conclusions

This work will transition into Phase 2 and the power plant side of the dynamic simulation will be expanded to include models of the boiler and heat recovery steam generation system to yield plant-wide dynamic simulations for sub- and super-critical, coal-fed power plants. These models will then be used in a variety of load-following scenarios to determine the mechanical stress caused by cyclic operation on existing power plants. The cumulative effect of the additional mechanical (and thermal) stress gives rise to additional operating and maintenance costs that will be evaluated. Optimal deployment strategies for one or multiple power plants will be developed that take account of the additional operations and maintenance costs.