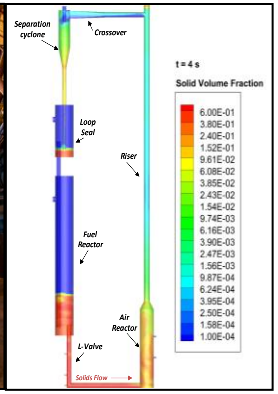
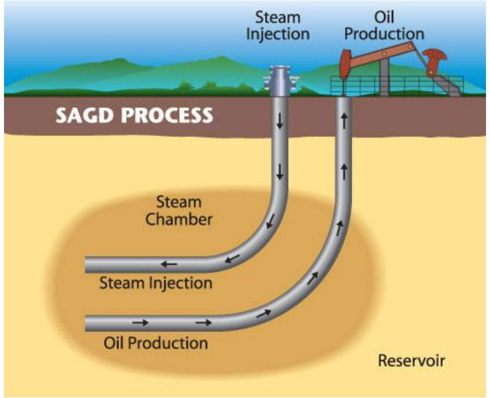
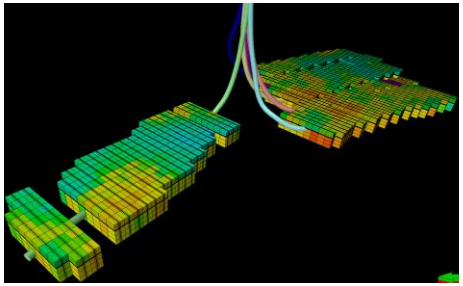
NETL





Source: Canadian Centre for Energy Information



Industrial Carbon Management Initiative (ICMI) – Chemical Looping Combustion

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Ronald W. Breault
ICMI/ARRA Project Manager

URS

U.S. DEPARTMENT OF ENERGY

Industrial Carbon Management Initiative

Innovative Options for Future Power

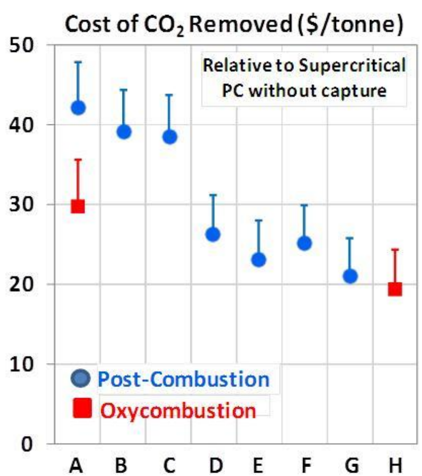
Industrial boilers: smaller size enables early application of low-cost carbon capture.

Smaller CO_2 volume can be used in EOR, *future* enhanced gas recovery, or converted to niche chemicals with renewable/waste energy.

ICMI Research Areas

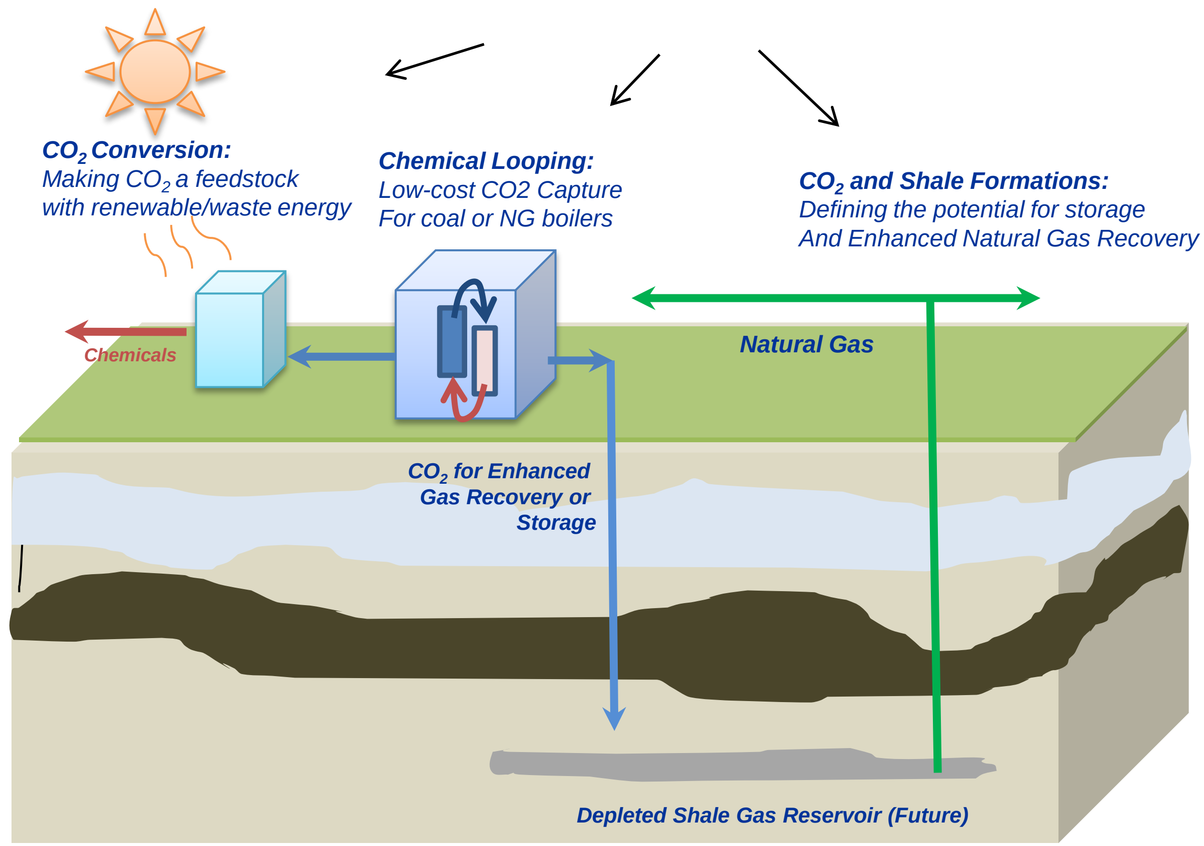
Comparison of CO2 capture costs

Chemical looping eliminates the need for air separation in oxy-fuel systems.



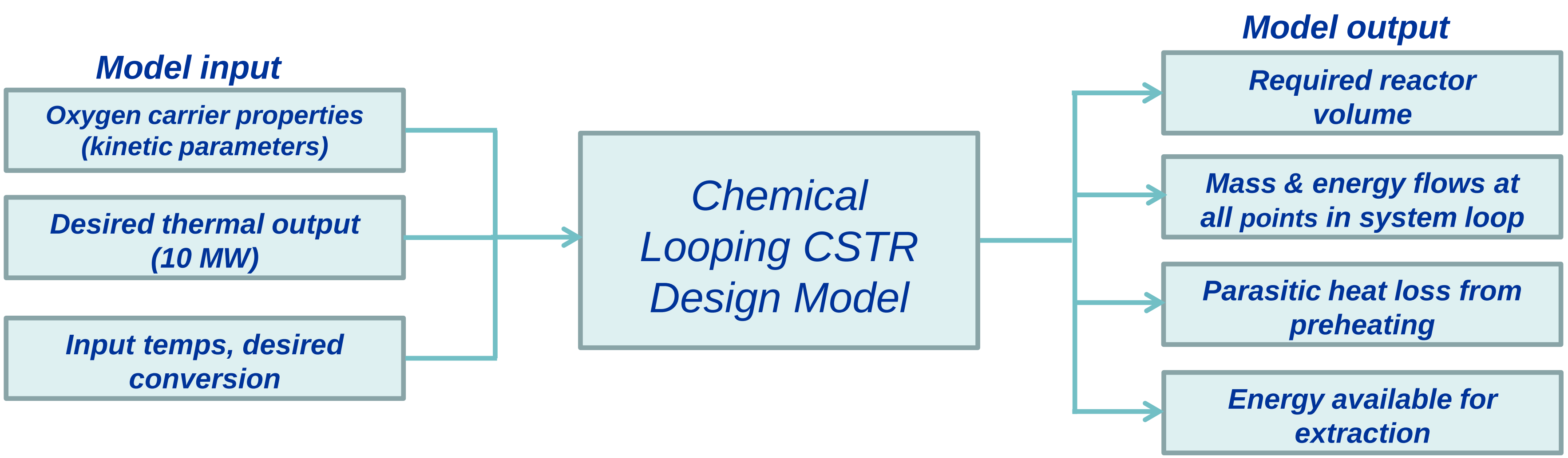
ICMI will quantify capture cost for Industrial applications

A – Supercritical PC w/Current Amine
B – Ultrasupercritical PC w/Current Amine
C – USC PC w/Amine + Adv. Compress
D – USC PC w/Advanced CO_2 Sorbent + Adv. Comp.
E – USC PC + Adv. CO_2 Membrane + Adv. Comp.
F – Adv. USC PC + Adv. Sorbent + Adv. Comp.
G – Adv. USC PC + Adv. Membrane + Adv. Comp.
H – Advanced Oxycombustion Power Cycles

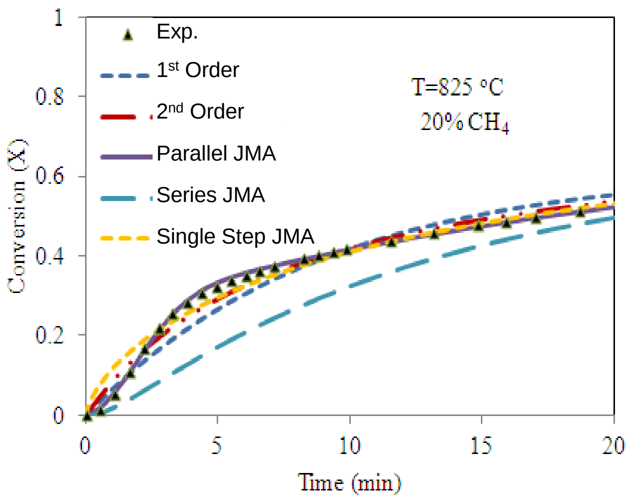


Carrier Screening Model

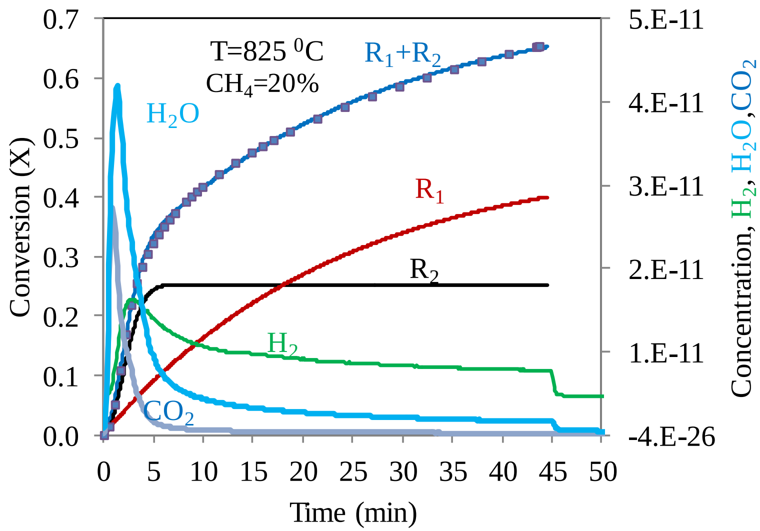
- Goal: Develop a simple model to estimate performance of various carrier materials in scaled Chemical Looping systems (10-100MW)
- Estimate reactor sizes, AR/FR Volumes, solids circulation rates using kinetic rate laws developed by NETL researchers
    - Compare scaled CLC systems to typical steam boiler systems
- Look at system tradeoffs, i.e. is it possible to decrease gas pre-heating without great losses in efficiency? How much useful heat can be extracted under scaled scenarios?
- Results will feed into techno-economic evaluation where the best end-use technology for CLC (steam generation for SAGD, EOR, etc.) will be selected
- Model uses reactor design equations for a Continuously Stirred Tank Reactor (CSTR), derived to include CLC reaction terms (Ex: R_o – oxygen carrying capacity)



Hematite Kinetics for CL



Best fit of kinetic data is parallel JMA reaction model



Solids conversion as a function of time, R_1 and R_2 show the speed and contribution of each reaction.

TGA kinetic testing was conducted in 2012 for reduction and oxidation of Hematite(Fe2O3). For reduction (with CH4), a parallel reaction mechanism was determined:

R_1: $Fe_2O_3 + CH_4 \rightarrow 2FeO + CO + 2H_2$

R_2: $12Fe_2O_3 + CH_4 \rightarrow 8Fe_3O_4 + CO_2 + 2H_2O$

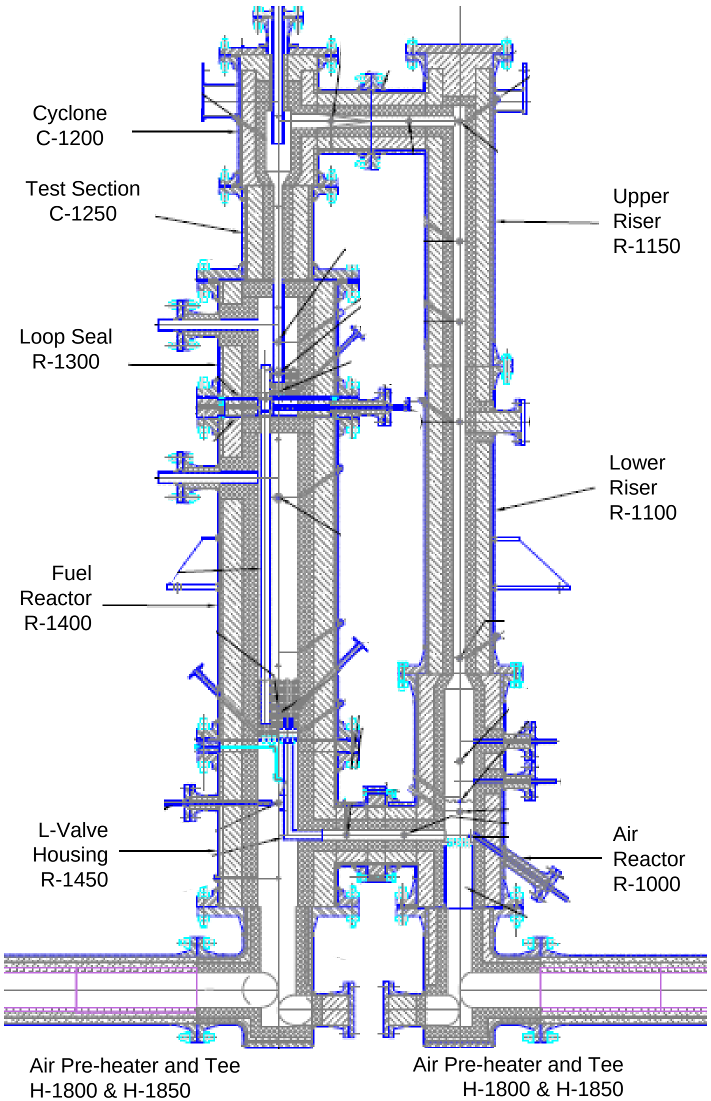
The interpretation of the kinetic mechanism and rate equations were determined from the data fit as well as mass spec analysis of products during reaction. The rate of solids conversion (X) with time, dX/dt, is based on the nucleation model and is described by:

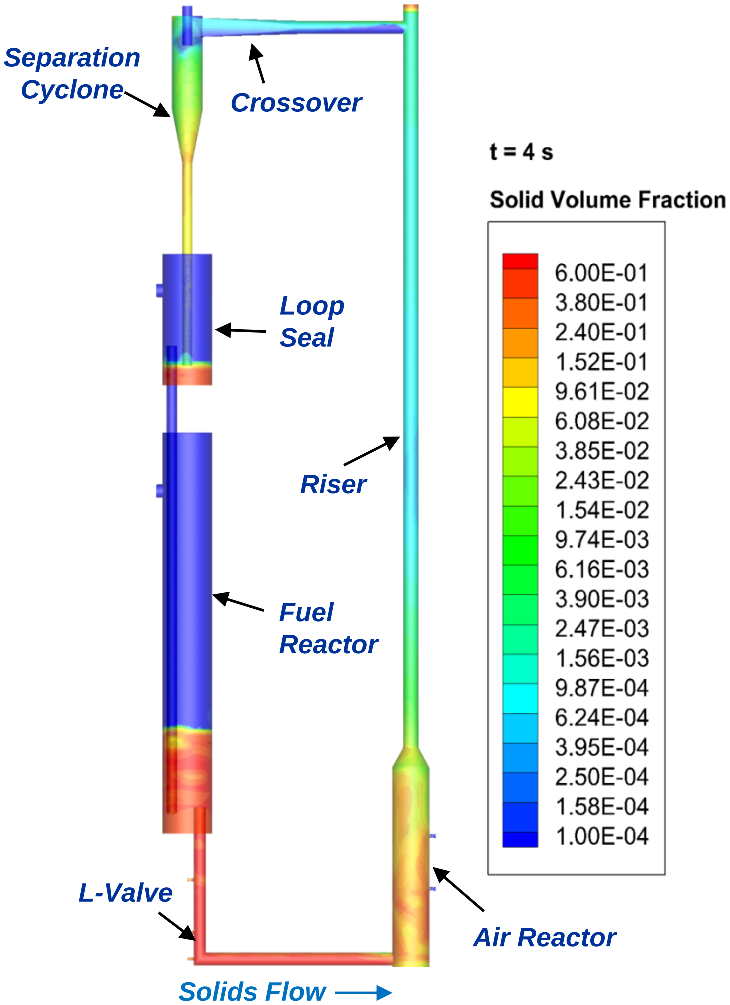
$$\left.\frac{dX_t}{dt}\right|_{R_1+R_2} = k_1\left(w_1 X_\infty - X_1\right) + 2k_2\left(w_2 X_\infty - X_2\right)\left(-\ln\left(1-\frac{X_2}{w_2 X_\infty}\right)\right)^{1/2}$$

where, $$k_2(1/\min) = K_2^{\frac{1}{n_2}} = A_2 e^{-\frac{E_2}{RT}}$$

Parameters such as *w*, X_∞, and *n* are the weighting factor of reactions R_1 & R_2, maximum conversion possible, and shape factors for nucleation.

High Fidelity Modeling of CLC in the CLR

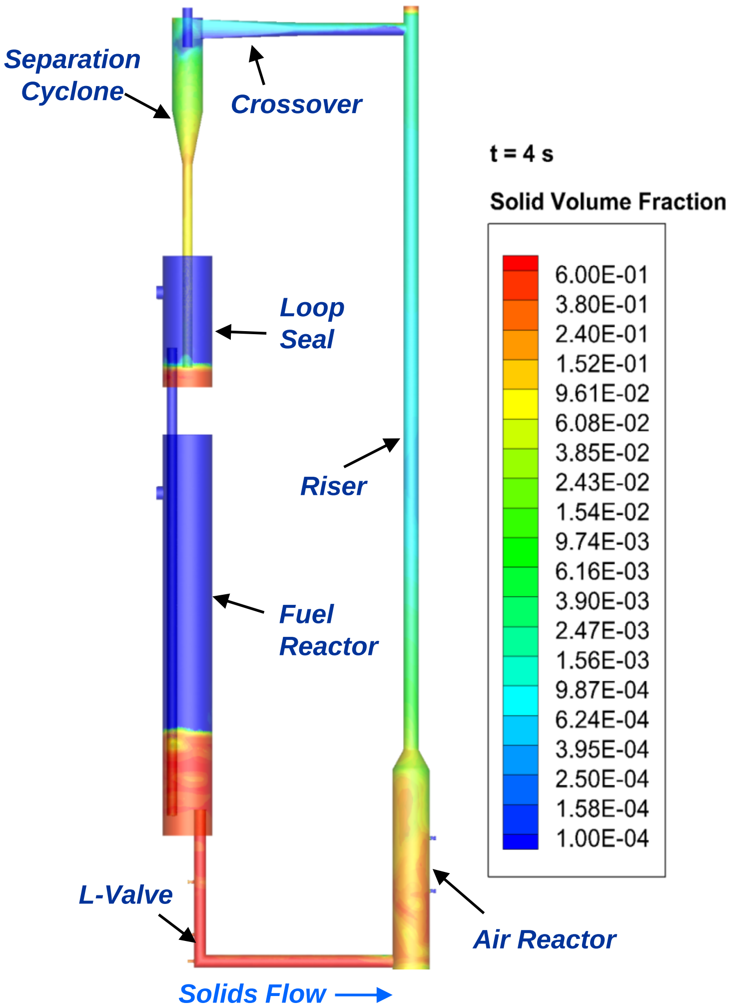




CLR whole system – 3D, front view

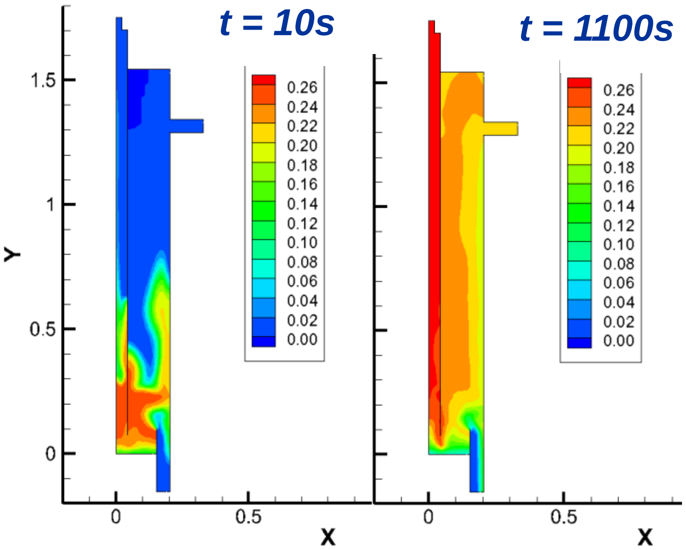
Modeling the Chemical Looping Process

- **Modeling Efforts & Goals:**
  - Developing models/simulations to study CFD of hydrodynamics (w/reactions) for CL oxygen carriers. Using several CFD codes:
    - FLUENT
    - Barracuda
    - MFIX (open source - NETL)
    - Open FOAM
  - Support & guiding experimental program
    - Models help to guide experimental test plan development by narrowing down important variables
  - Verification & Validation
    - Working to validate models as experimental data becomes available
    - Includes tuning submodels (friction, turbulence) to more closely match reality, so that experimental and simulations results align
  - Evaluate conceptual designs for scale-up, look at cases involving fuels such as coal



CLR whole system – 3D, front view

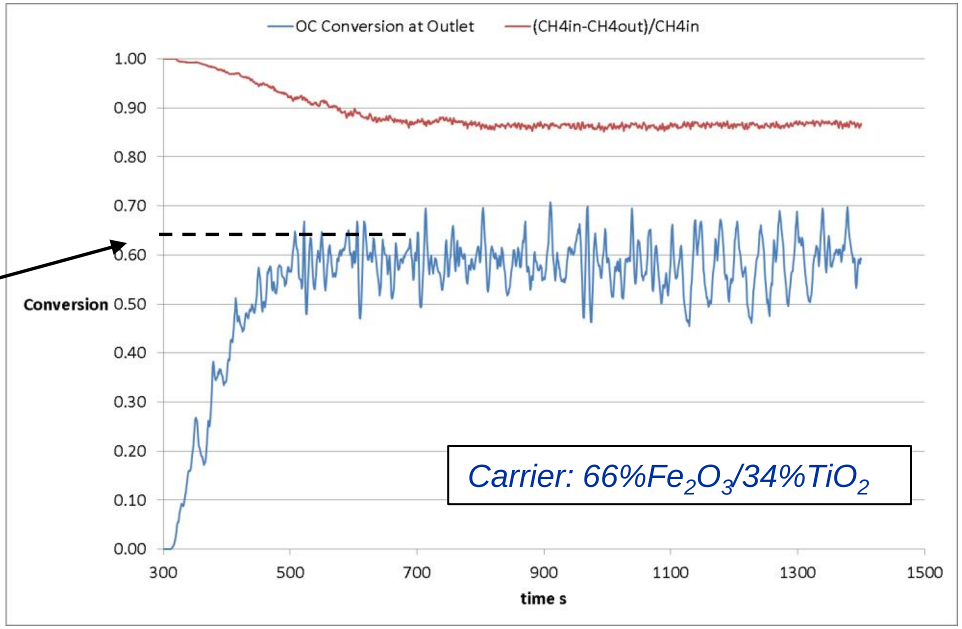
Initial 2D and 3D Reacting Simulations Completed



CLR Fuel Reactor - CO_2 mass fraction

- *Using early kinetic data from literature (ilmenite)*
- *Completed a sensitivity analysis on fuel conversion*
  - *Solids inventory (bed heights: 8, 12, 16 inches)*
  - *Solids circulation rates (800-1600 lbs/hr)*
  - *Fluidization gas flow rates*
  - *CH_4 concentrations (10, 15, 25, 100%)*
  - *Temperatures (1150-1225K)*

8-inch bed height with 800 lb/hr circulation rate predicts 86% conversion of fuel.
CLR was designed for 12-inch bed height and simulations predict >99% fuel conversion for these conditions.

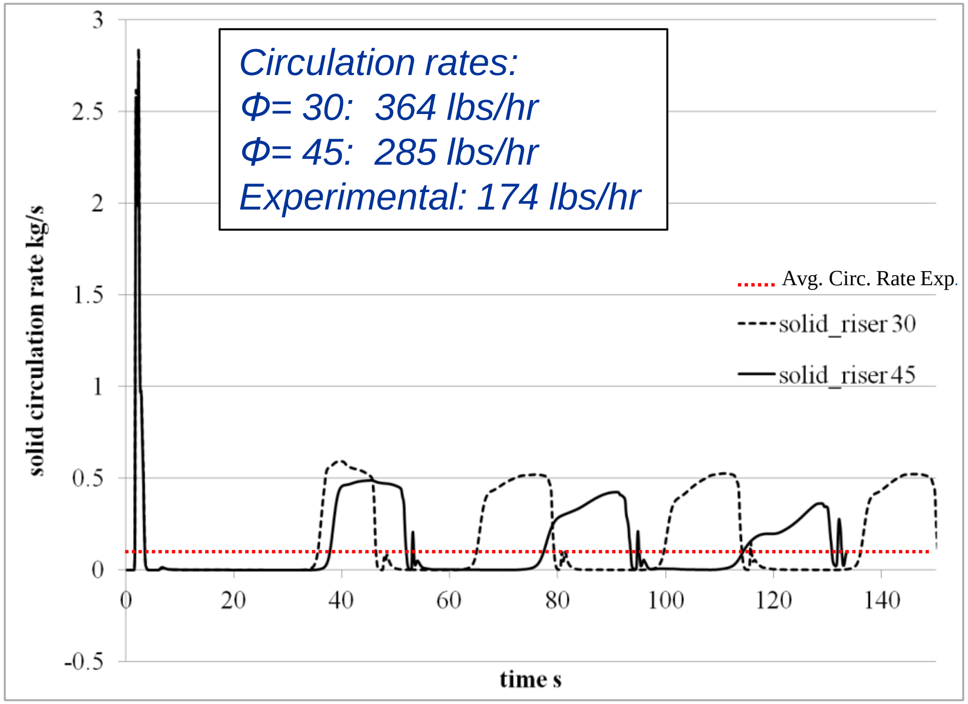


Summary of Experimental/Modeling Efforts

Simulation Geometry	Dimensions	Type of simulation	# of Variants	CFD Code used for simulations
Cold Flow Unit	3D	Hydrodynamics only	4 separate cases to match exp. conditions	Fluent, OpenFOAM
Single Fluid Bed	2D, 3D	Hydrodynamics w/ kinetics	w/Kinetics: Abad[1] Monazam[2]	Fluent, OpenFOAM
Fixed Bed	2D	Hydrodynamics w/ kinetics	w/Kinetics: Abad[1] Monazam[2]	Fluent, OpenFOAM
CLR (full loop)	3D	Hydrodynamics w/ kinetics	w/Kinetics: Abad[1,3]	Fluent, OpenFOAM Barracuda
CLR (Separate Fuel Reactor)	2D, 3D	Hydrodynamics w/ kinetics	w/Kinetics: Abad[1,3]	Fluent, OpenFOAM

[1] Abad, et al. Chem. Eng. Sci. (2011)
[2] Monazam, et al. Energy & Fuels, (2012) – in review
[3] Abad, et al. Chem. Eng. Sci. (2007)

Cold Flow Unit – Exp. vs. Simulation Results



Modifying the friction submodel has helped to dampen the oscillations in the simulations and created a 50% improvement in matching the average simulated versus experimental circulation rates.

Friction is calculated by the following:

$$\mu_s = \mu_{s,col} + \mu_{s,kin} + \mu_{s,fr}$$

$$\mu_{s,fr} = \frac{P_s \sin(\phi)}{2\sqrt{I_{2D}}}$$

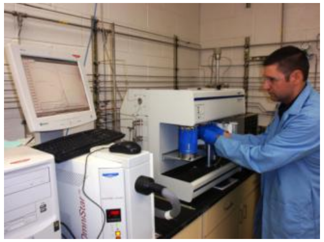
Where Φ is the internal friction angle. Friction angles of 30 and 45 degrees were evaluated.

Average pressures show good similarity between simulations and experiments in various parts of the cold flow unit.

Pressure location	Simulation Avg. pressure (in H_2O)	Experimental Avg. pressure (in H_2O)
Air Reactor	14.97	15.85
Fuel Reactor	20.03	20.62
Loop Seal	5.45	4.05

Experimental Units

Carrier Screening Tests



TGA and Mass-Spec

Lab-scale Fixed Bed Reactor

Small Batch Evaluation Tests

Attrition Test ASTM D5757

Single Fluidized Bed Reactor

Large Batch Evaluation Tests

Integrated Cold Flow Unit

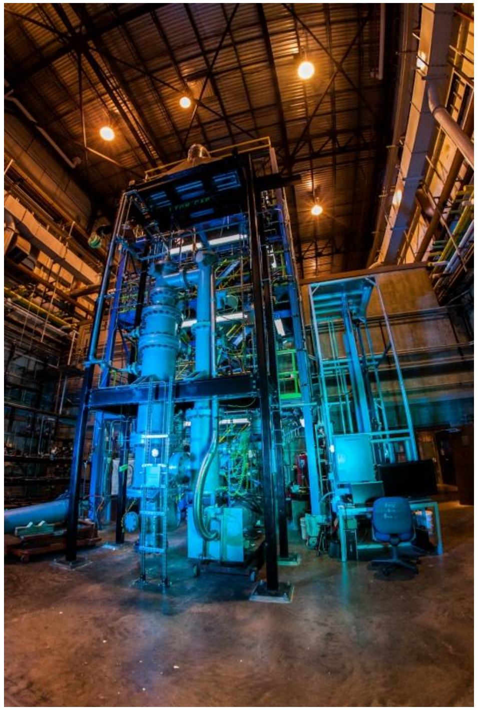
Integrated Reacting Unit

External Carrier Manufacturer

Small Batch

Large Batch

Experimental/Modeling Efforts



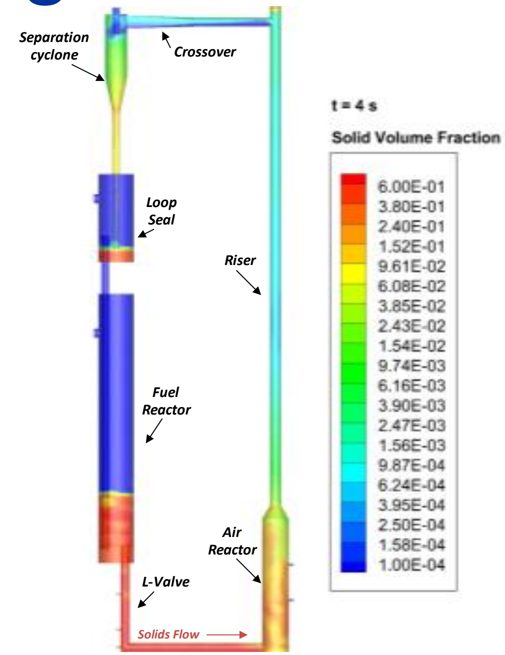
Integrated Reacting Unit

Fuel Conversion
CO_2 leakage

Solids Circulation Rates

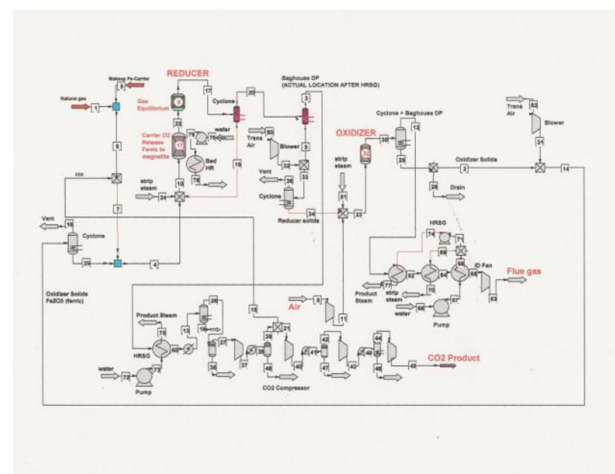
Process Design Inputs/Outputs

Attrition Resistance

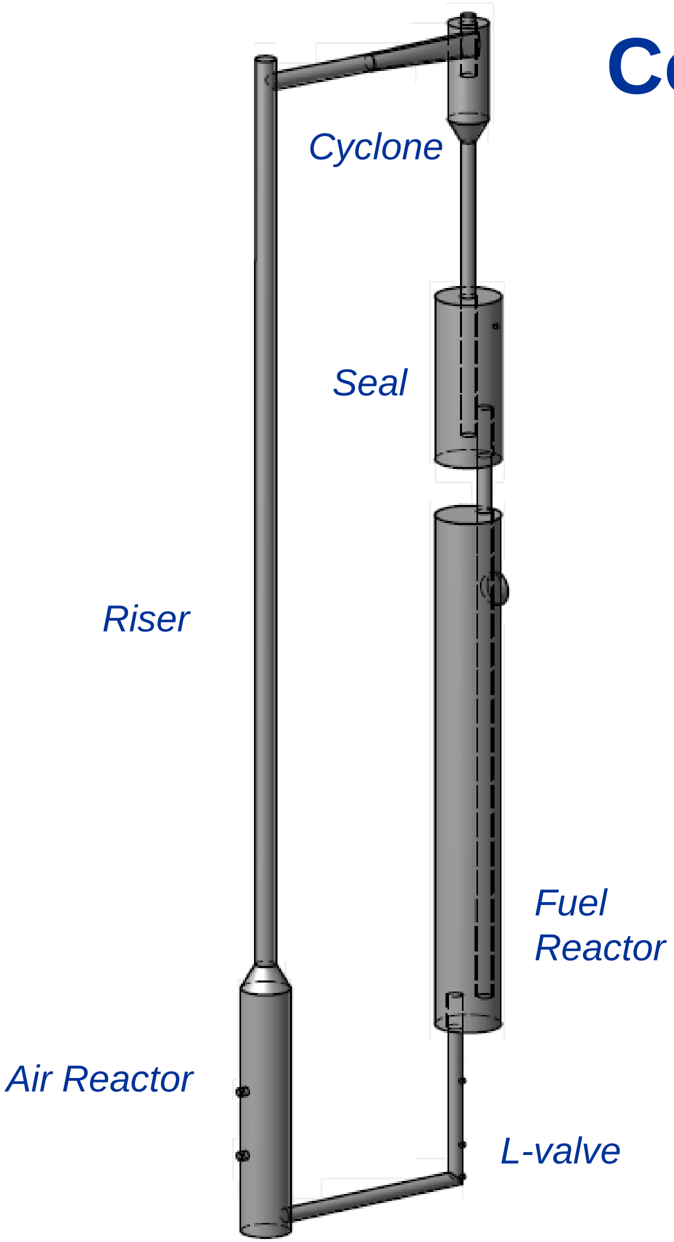


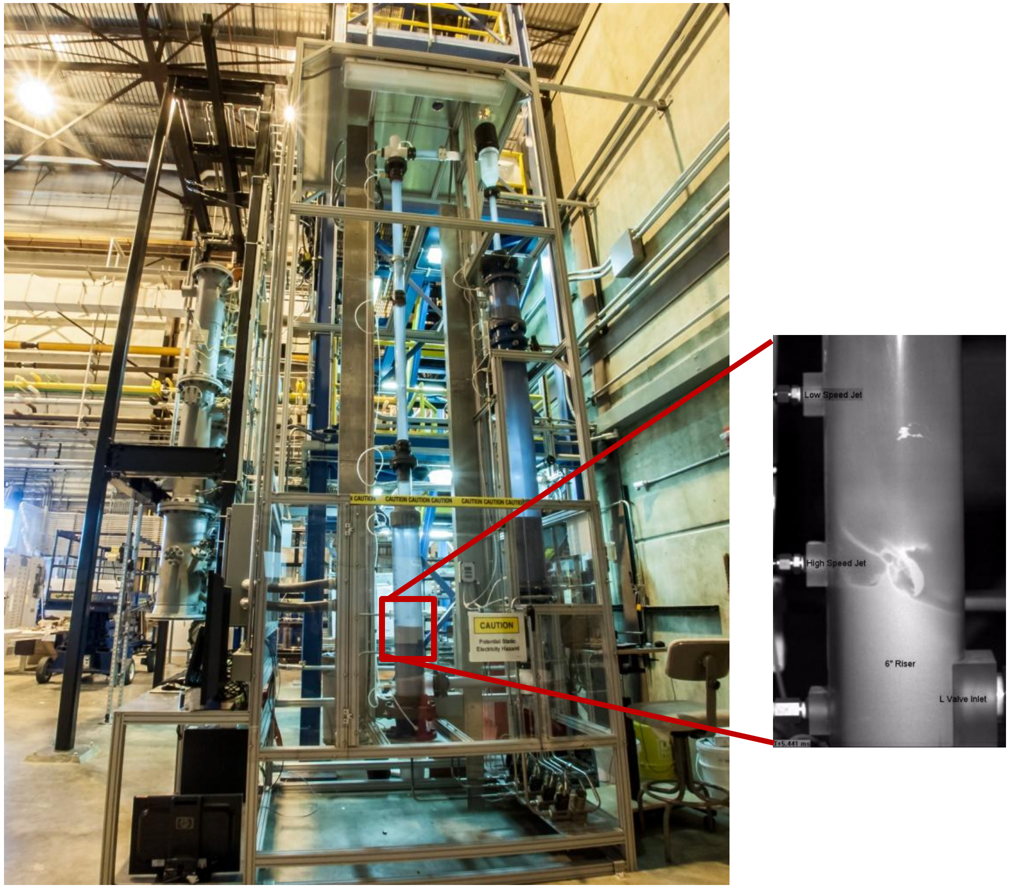
Attrition Test ASTM D5757

Attrition Resistance



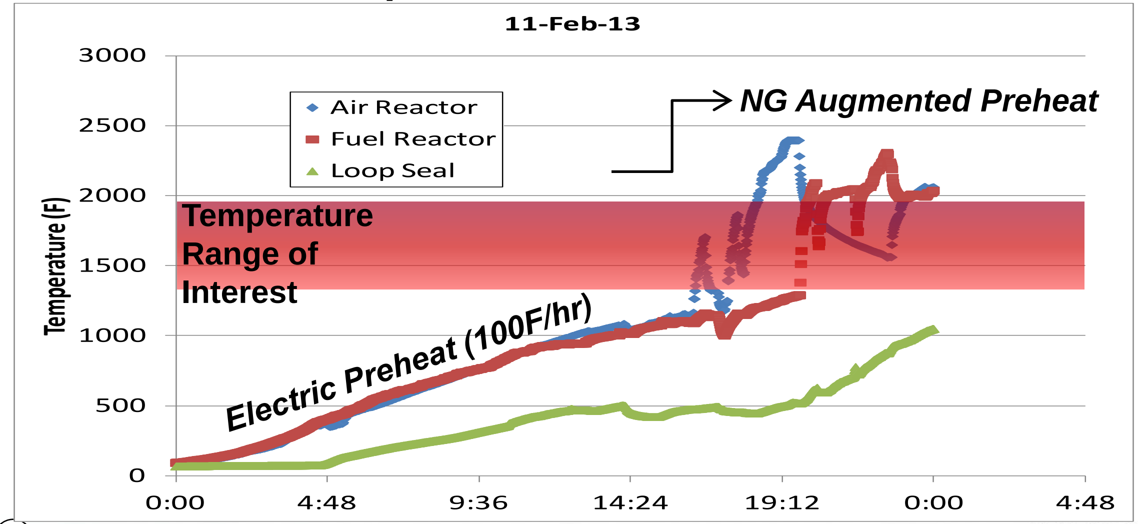
Cold Flow Unit Is Operational





Chemical Looping Reactor

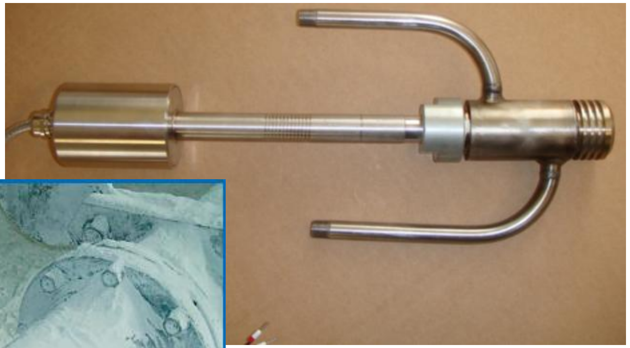
- Potential range of operating temperatures is better than expected
- Operation at elevated pressure (20-30 psig) has been demonstrated in the electrical preheat mode
- Operating temperatures in excess of 1000C have been demonstrated in both the air and fuel reactors
- Carrier addition/makeup procedure will be improved
- Demonstrated solids heating and transport from air reactor to loop seal



Microwave Solid Circulation Sensor Results Are Encouraging

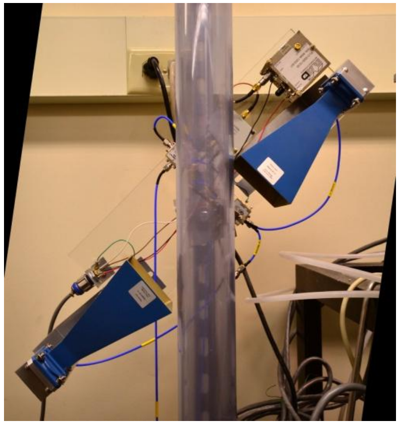
Commercial Sensor (SWR)

- 1st or 2nd high temperature unit built
- Uses single sensor oriented normal to flow path
- Calibration efforts underway
- Normal operation 200°C



CMU Sensor Development

- Sensor is not normal to flow path
  - Doppler shift
- Single sensor (and pitch-catch sensors) are evaluated
- Encouraging results on single particles and realistic particles



Technical Challenges in Carrier Development

Challenges

- *High reactivity*
- *Low fragmentation and attrition*
- *Low tendency for agglomeration*
- *Low cost and environmentally benign*
- *Objective: develop new oxygen carriers with better reaction activity, less agglomeration and stable performance during cyclic tests*

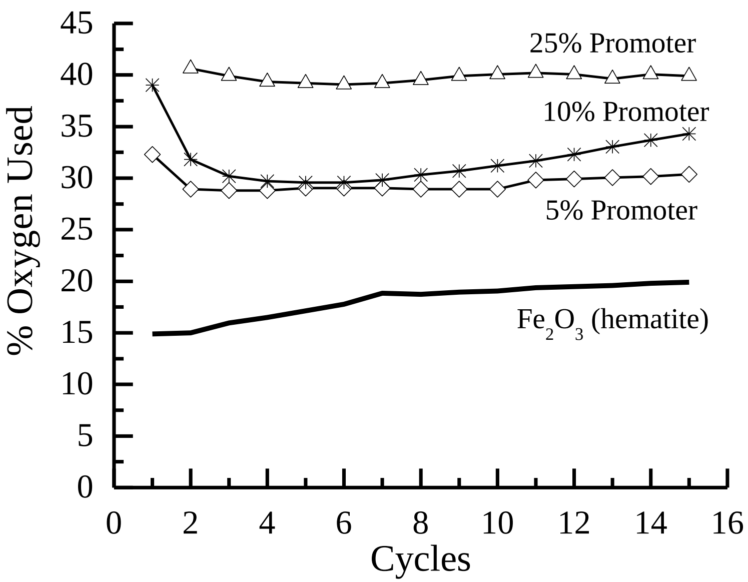


Figure 2 *TGA analysis on the Percentage O_2 utilized for the CLC reaction of methane over hematite and promoted hematite oxygen carrier; 15 reduction-oxidation cycles at 800 °C.*

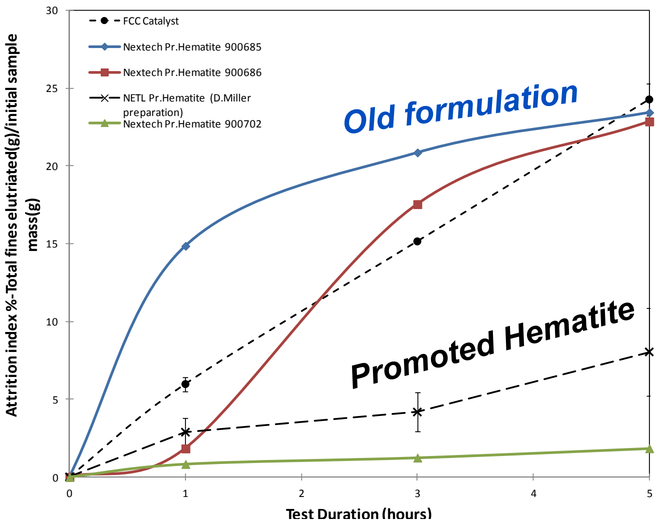


Figure 1 *Attrition analysis on the hematite and various formulations of promoted hematite oxygen carriers. Comparison is made to a standard FCC catalyst under the same operating conditions.*

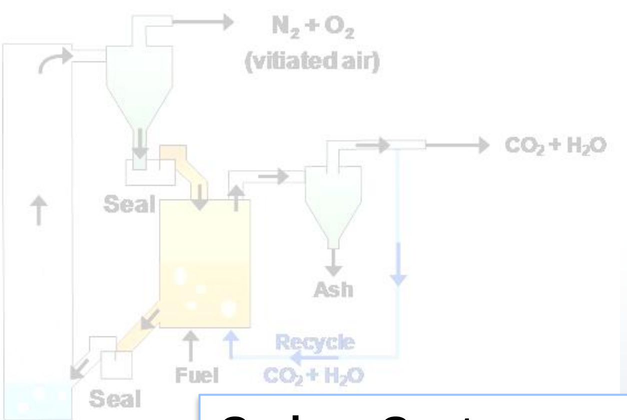
Achievements

Our Fe-Cu and promoted oxygen carriers show:

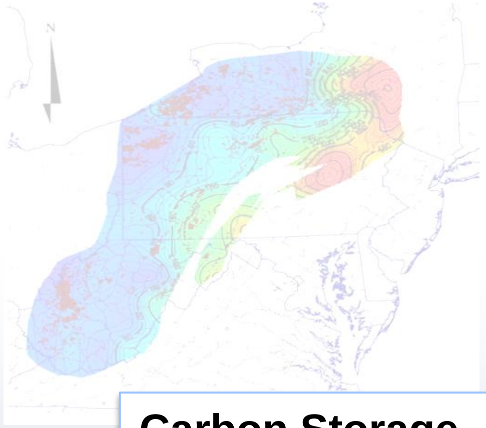
- *Improved carrier reactivity*
- *Improved oxygen transfer capacity over the pure hematite carrier*
- *Good attrition characteristics*

ICMI Research Areas

Focus is on "industrial" applications: NG or coal boilers, process heat, chemical production, others. Technical results expected to benefit coal power as well.



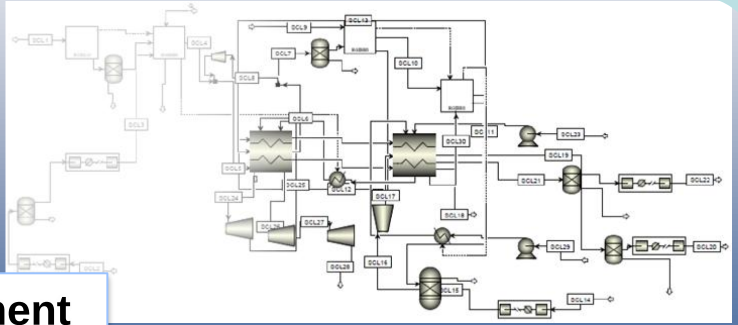
Carbon Capture
Chemical Looping Combustion



Carbon Storage
Depleted Shale Fields

Carbon Utilization
Photocatalytic Conversion

CCUS for Industrial Applications



Industrial assessment and systems analysis

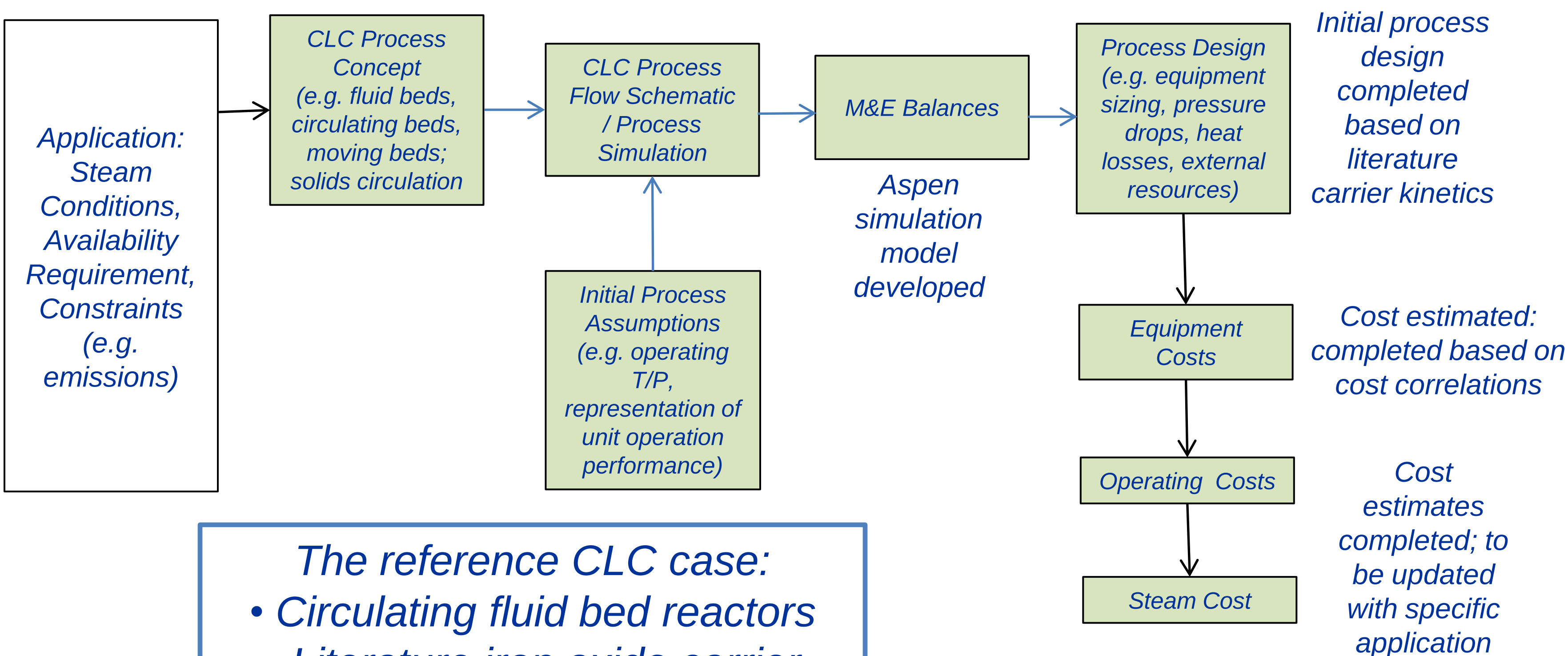
Techno-Economic Analysis

- **Objectives**
  - Develop design basis and methodology for industrial boiler system studies
  - Project performance and cost for conventional natural gas industrial boiler with capture (today's technology)
  - Develop plant system model for chemical looping combustion industrial boiler and estimate plant performance and cost
- **Use system analysis results to**
  - Compare conventional natural gas industrial boiler with capture and chemical looping combustion boiler with capture
  - Inform R&D program (e.g. applicable test conditions and performance goals)

CLC Analysis Overview

Steam Generator Capacity

- *27,500 lb/hr (~10 MW Thermal) and 275,000 lb/hr (~100 MW Thermal)*
- *600 psi with 100 F of superheat steam*



The reference CLC case:
- *Circulating fluid bed reactors*
- *Literature iron oxide carrier kinetics*

Sensitivity Analyses – Initial Findings

- **Plant capital cost represents ~ 10% of steam cost; fuel and variable operating costs represent ~90%**
- **CLC reactor vessels (i.e., reducer and oxidizer) estimated to represent ~ 9% of the plant capital**
- **Thus, developing reactor designs, with high reliability and modular design capability, represent a development program priority**
- **Capital cost reduction is important; potential opportunities will be evaluated by conducting integrated system analysis**
  - e.g. incorporate effect of selected set of changes (e.g. increase reactivity, carrier conversion and NG conversion) to understand costs for all affected system components.

Summary for Chemical Looping

- CLC focused on industrial applications
- Low and High Fidelity Models Developed to Advance Technology
- Models populated with parameters from experimental data
- Simulation results will be compared with test data on integrated CLR
- Successful oxygen carrier development at NETL
- Results feed into techno-economic evaluation

Back Up

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL

Team Members

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Dan Soeder, NETL ORD, Geologist

Image from: *Dan Soeder (2011)*

ICMI - CO_2 Storage in Depleted Shale Gas Reservoirs

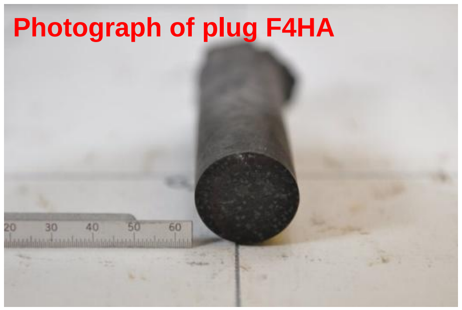
- Experimental work
- Reservoir simulation
- Techno-economic screening

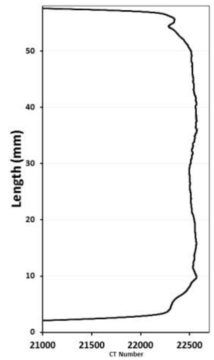
NETL-RUA
Regional University Alliance

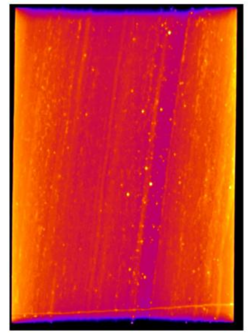
U.S. DEPARTMENT OF ENERGY

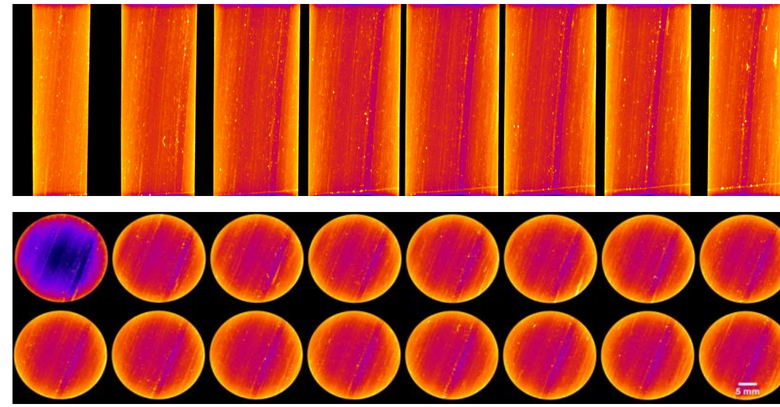
Experimental Results: Cores/Plugs

Computed Tomography: *Imaging a non-calcareous black shale with core plug oriented sub-parallel to bedding (sample F4HA)*

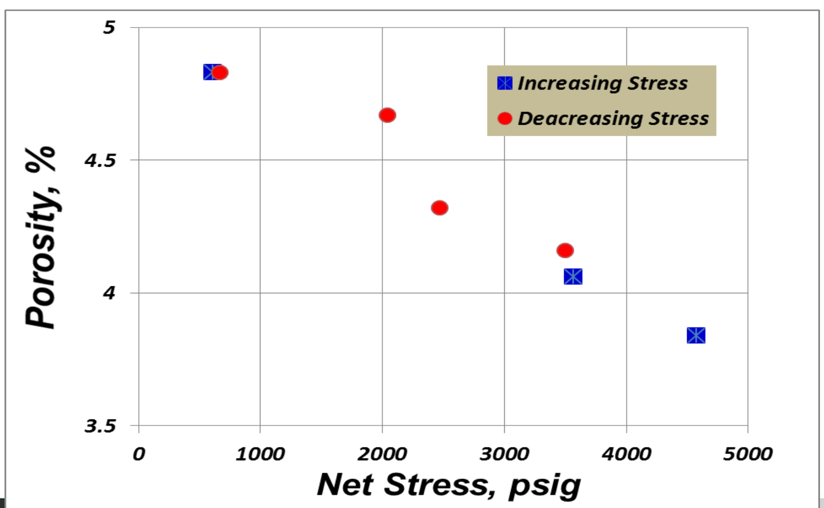


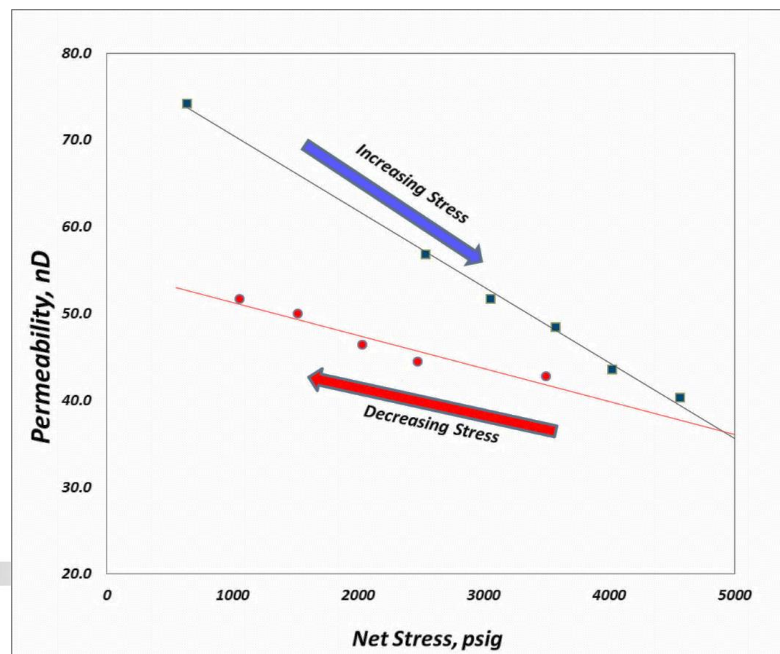






Petrophysical Analysis: *Matrix porosity and permeability as function of net stress in an shaley limestone (sample F2HA)*

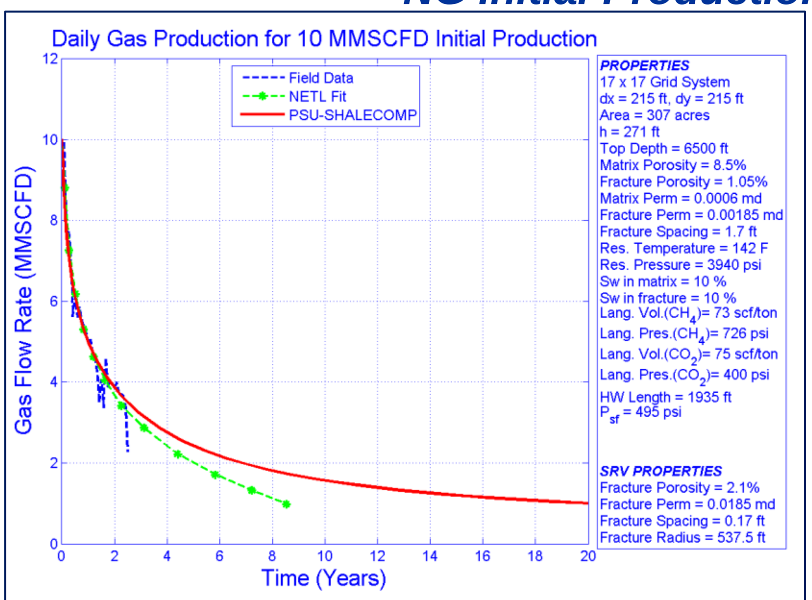


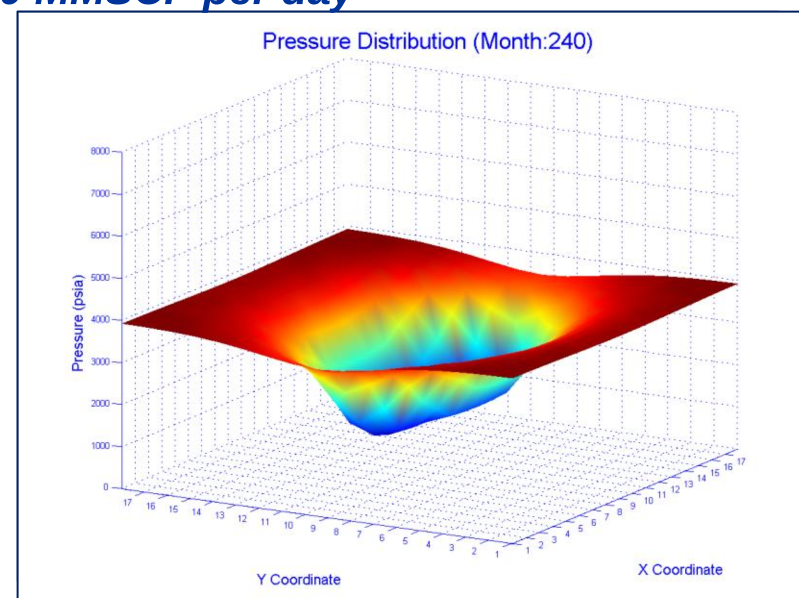


SHALECOMP model (Ertekin, PSU)

- **Dual porosity, dual permeability, compositional model for fractured low permeability reservoirs**
- **Apply model data from ICMI DBD for history match on single lateral production for inter-model comparison**
- **Move forward with CO_2 storage and EGR scenario evaluation**

Single lateral, ~3000 ft stimulated lateral length
NG Initial Production at 10 MMSCF per day

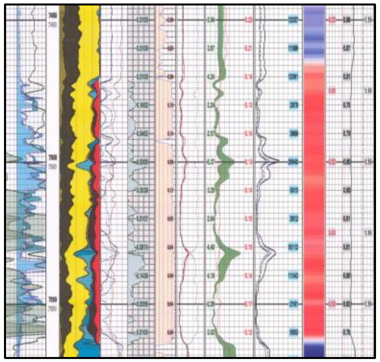




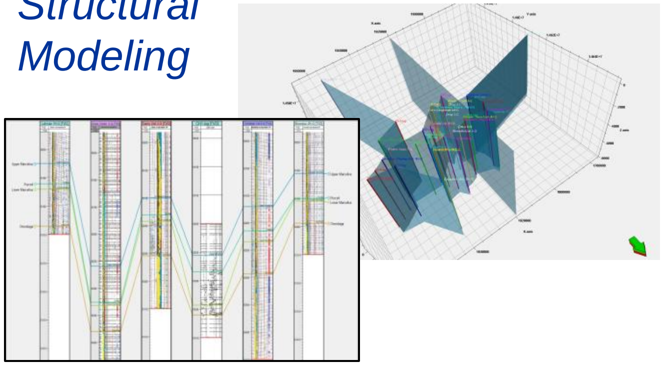
Content Contributed by: Turgay Ertekin, Penn State University Department of Energy and Mineral Engineering

Geo-modeling to Simulation workflow-Marcellus Shale

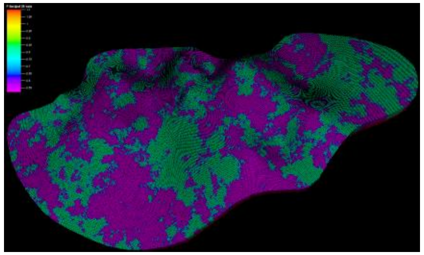
Well Logs



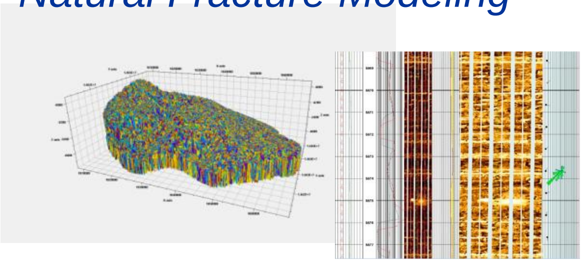
Structural Modeling

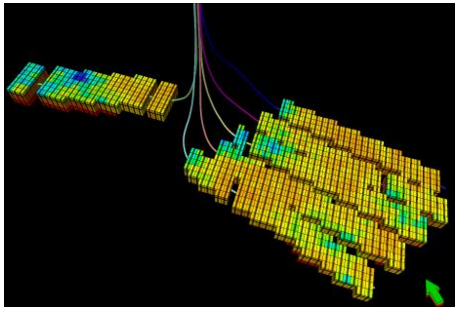


Property Modeling

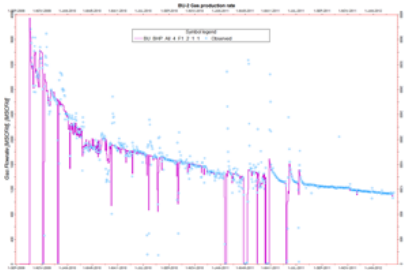


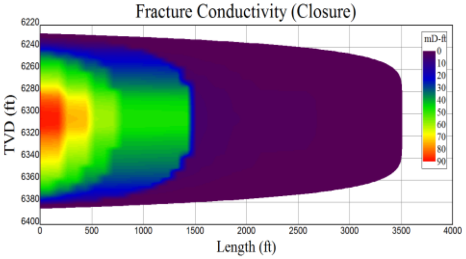
Natural Fracture Modeling





Hydraulic Fracture -LGR





HF treatment modeling

History matching

WestVirginiaUniversity.
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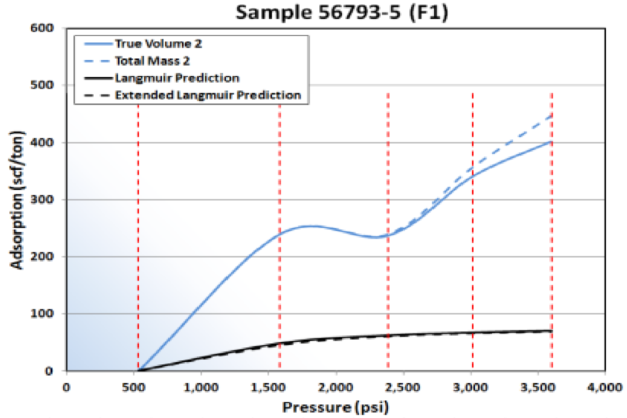
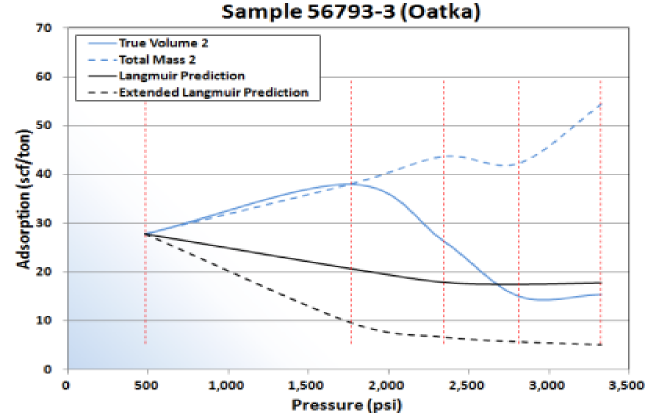
Sand face pressure for CO2 injection rates stcf/day (t = 30 years when injection ceases)

CO_2 Storage in Depleted Shale

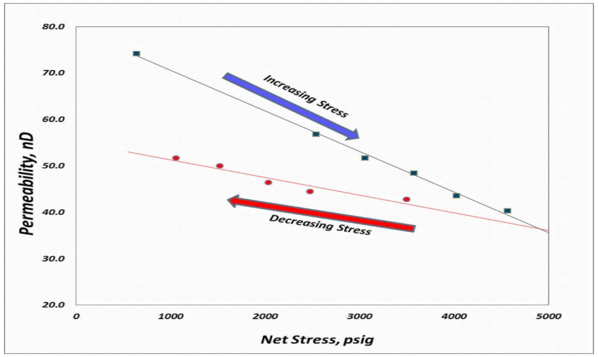
ICMI Mixed-gas Isotherms
Total CO_2 Adsorbed at Each Step



ICMI Mixed-gas Isotherms
Total CH4 Adsorbed at Each Step

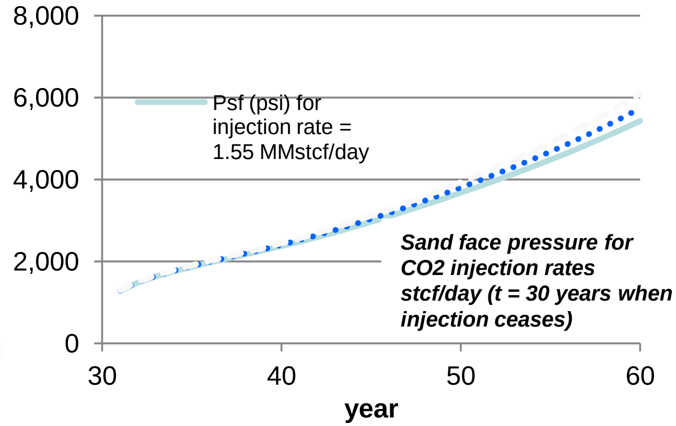


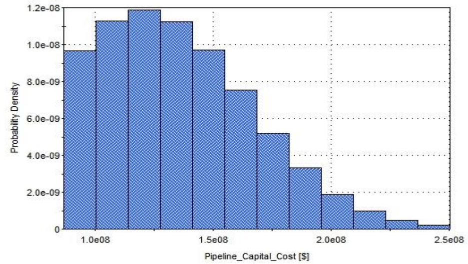
Mixed gas isotherms will be used to determine the relative attraction of CO2 vs. CH4 to shale, and will be used in numerical models to determine displacement of CH4 by CO2 leading to an assessment of enhanced gas production.



Impact of net stress on the average permeability of a shale were measured and factored into simulations of depletion of a reservoir and injection of CO2. Largest net stress (greatest depletion) at which permeability will be irreversibly reduced is critical.

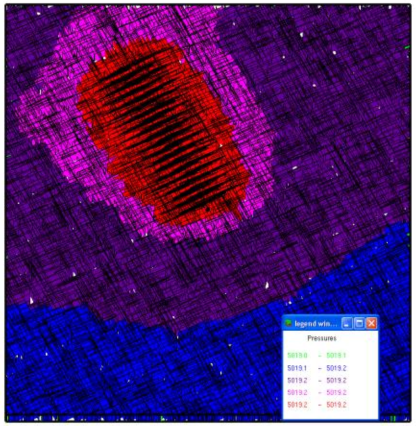
Graphs left and below tie in the physical tests, their use in the model and economics: tests feed the model, model yields parameters such as injection pressure, and pressure plus source –to-sink relationships yield economic assessment.





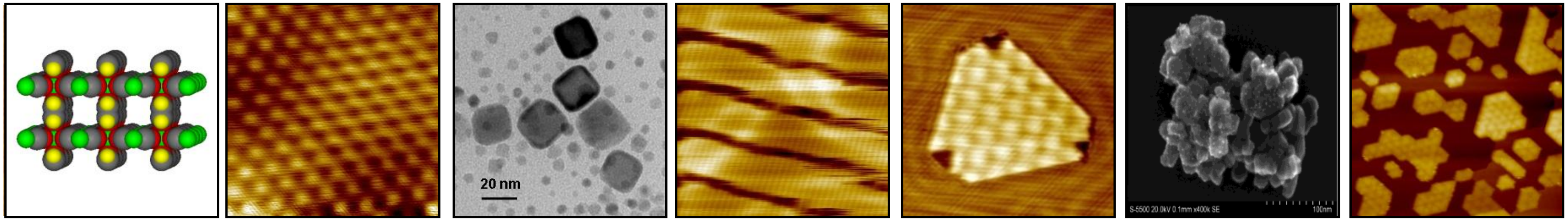
Capital cost for building CO2 pipeline based on estimated tortuosity

Marcellus NE area



2D view of FracGen/NFFlow realization for Marcellus shale. Engineered hydraulic fractures are introduced into a network of pre-existing natural fractures. NETL-ORD is simulations the interaction between CO2 and natural gas shale to determine storage and enhanced gas production.

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY



CO_2 Conversion Catalysts

U.S. DEPARTMENT OF ENERGY

Fundamental Surface Science Approach

Adsorption Configuration

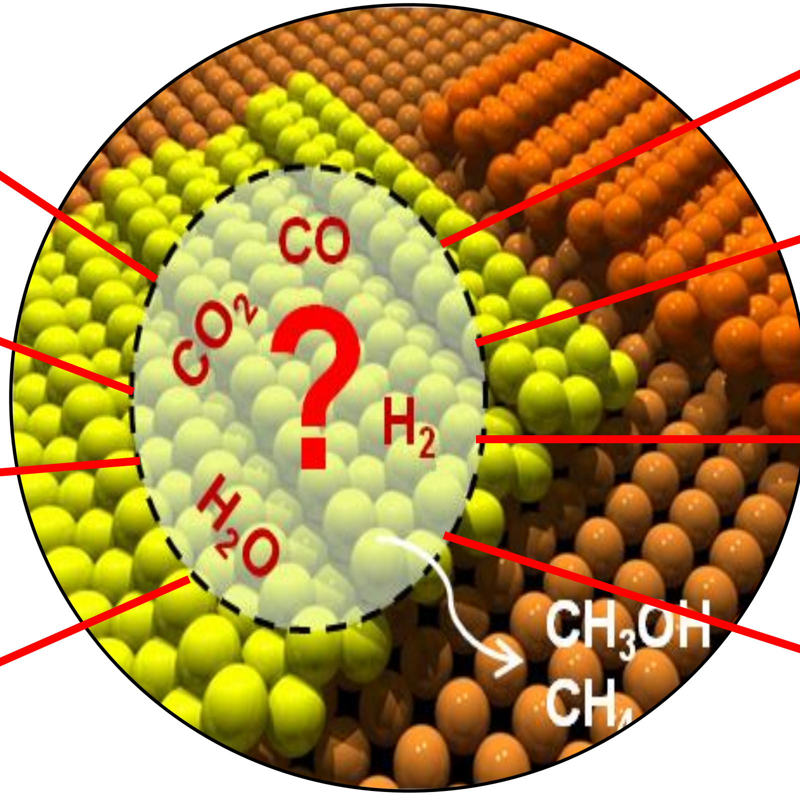
Rxn Energetics

Diffusion

Binding Sites

Rxn Intermediates

Intermolecular Interactions



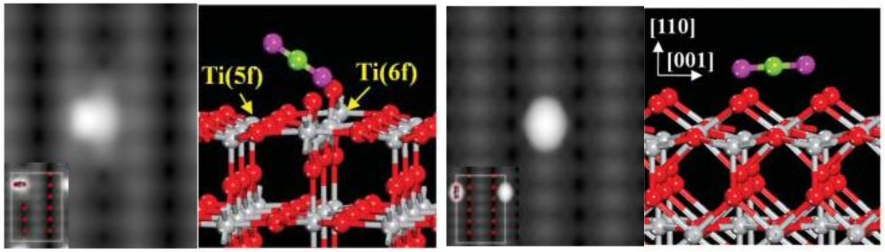
Role of Defects

Testing & Developing New Computational Methods

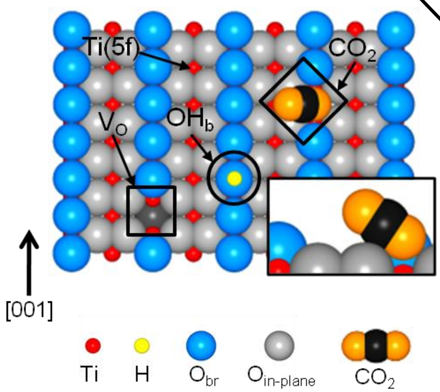
New Dispersion Corrected DFT Method Implemented by NETL-RUA (Jordan/Sorescu) Improve Agreement Between Experiments and Theory

Identifying Adsorption Sites and Diffusion Barriers of CO_2

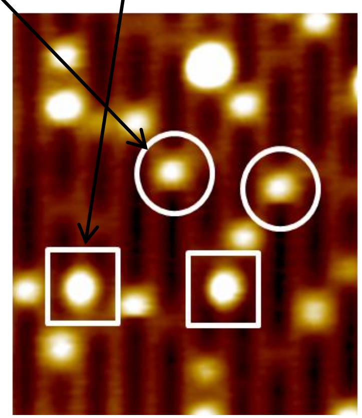
DFT Theoretical Determination of CO_2 Adsorption Configurations



Tilted @ Defect **Flat on Ti Row**



Experiment

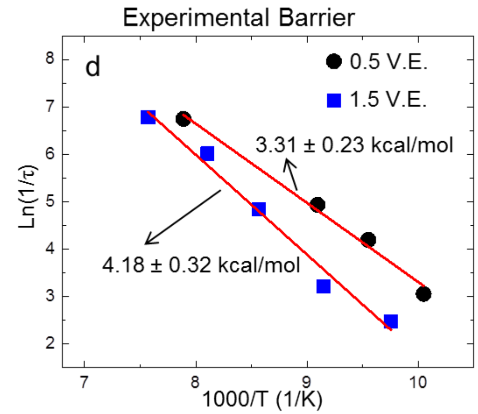


The most stable configuration: CO_2 at V_O (10.21 kcal/mol)

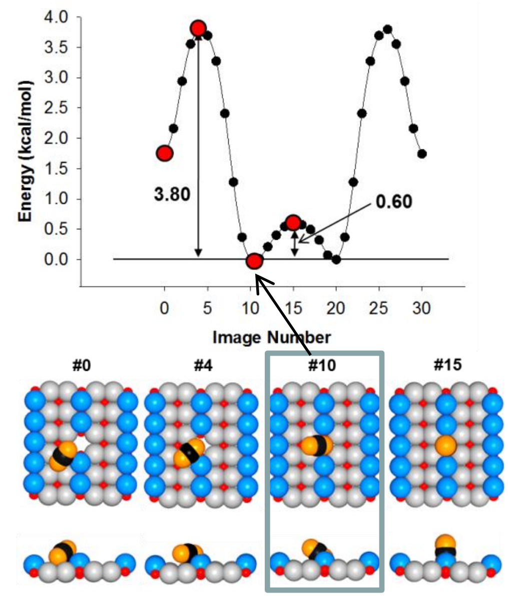
STM image
CO_2 / TiO_2(110)

Sorescu et al. *J. Chem. Phys.* **134**, 104707 (2011)

Measurement *and* Modeling of CO_2 Diffusion Kinetics



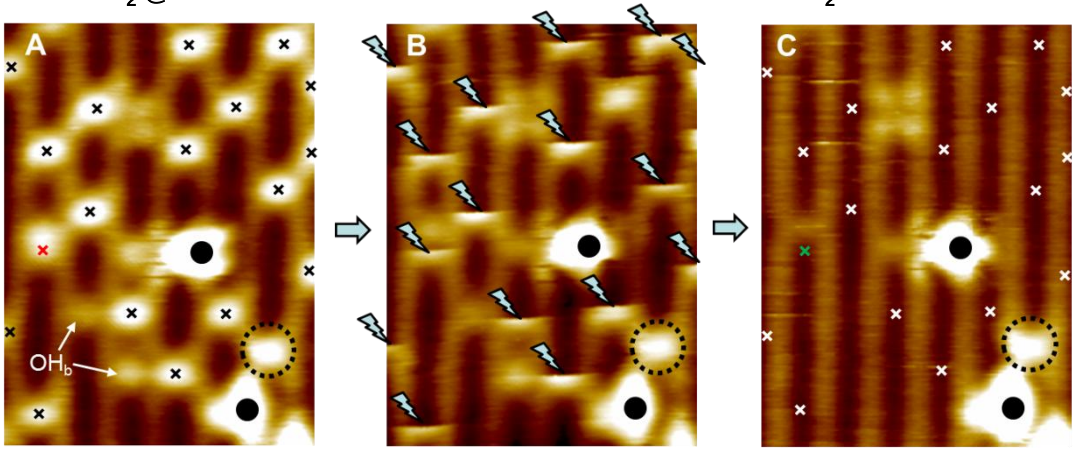
Theoretical Barrier (DFT, CI-NEB)



Lee et al. J. Phys. Chem. Lett. ***2****, 3114 (2011)*

Identifying Dissociation Mechanism of CO_2

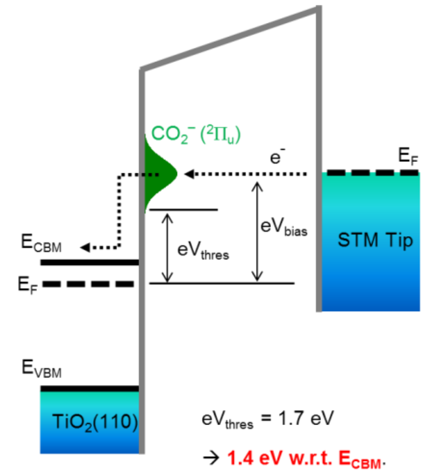
CO_2 @ Defects | **STM Pulse** | **CO_2 desorbs as CO**



Prior to pulsing (CO_2@V_O) | **Pulsing during scanning (Half of CO_2 visible)** | **After pulsing (V_O healed, No CO_2, CO, O found)**

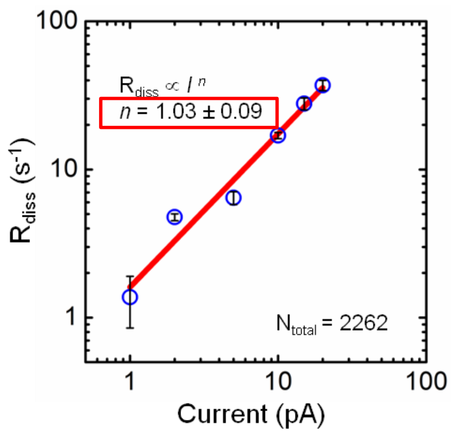
Formation of negative CO_2 ion is <u>the key first step</u> for CO_2 activation.

Schematic Energy Diagram

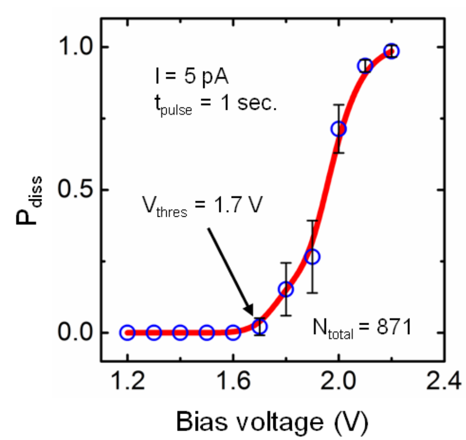


Electron acceptor level of CO_2 lies 1.4 eV above the conduction band minimum.
– An important guide for photocatalyst engineering.

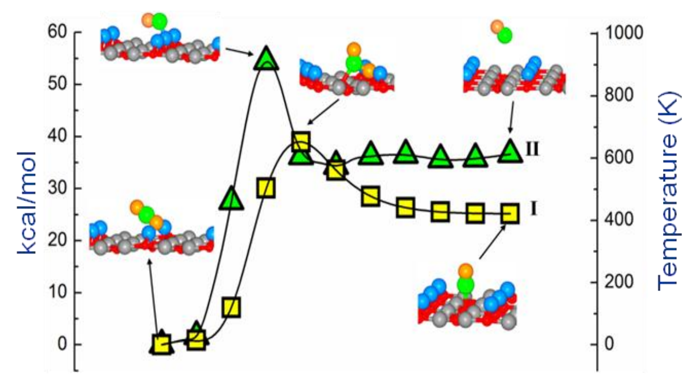
# of e$^-$ associated



Energy dependence



Theoretical Thermal Activation Barriers



*Lee et al. J. Am. Chem. Soc. **133**, 10066 (2011)*