NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL-ORD Chemical Looping Coal Combustion Research

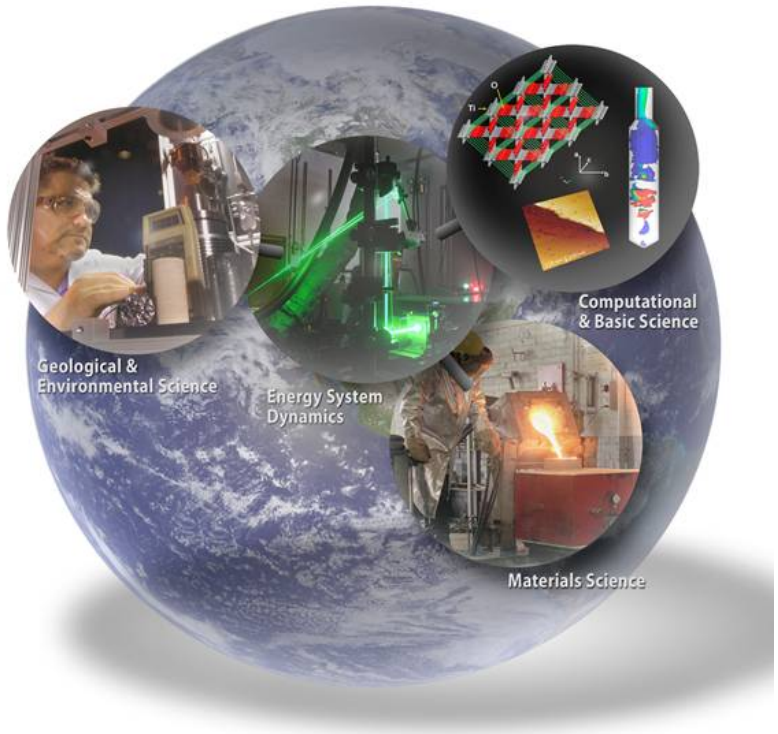
NETL CO_2 Capture for Existing Plants R&D Meeting

March 25, 2009

U.S. DEPARTMENT OF ENERGY

NETL Office of Research and Development

- **NETL In-House Research and Development Organization**
- **Tackling important national energy problems –**
  - CO_2 management, energy security, advanced fuels development, hydrogen technology, hybrid cycles, mercury capture, hydrates
- **Capitalizing on unique facilities and capabilities**
  - History dates to early 1900's
- **Achieving breakthrough science-**
  - Computational science and application, hydrogen technologies, combustion science and engineering, sequestration mechanisms
- **Achieving technology successes –**
  - R&D 100 awards, technology transfer awards, publications, licenses, etc.
- **Four Focus Areas of Research**
  - Computational and Basic Sciences
  - Energy System Dynamics
  - Geological and Environmental Science
  - Materials Science



Overview

- **Portfolio of FY09 Research Projects**
  - Projects will continue into FY10 and FY11

- **Participants in the NETL/ORD Chemical Looping Coal Combustion (CLCC) Program**
  - NETL/ORD Federal Researchers
  - West Virginia University
  - Carnegie Mellon University
  - Research and Development Solutions, LLC
    - NETL Site Support Contractor
  - ANSYS, Inc.
    - NETL Support Contractor
  - REM, Inc.
    - NETL Support Contractor

Overview

- **Project Portfolio**
  - Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal
    - Ranjani Siriwardane (DOE/PI); Hanjing Tian (RDS); Tom Simonyi (RDS)
  - CFD Modeling of Chemical Looping Coal Combustion
    - Dave Huckaby (DOE/PI); Tom O'Brien (DOE); Kartik Mahalatkar (ANSYS); John Kuhlman (WVU)
  - Chemical Looping Process Simulation
    - Steve Zitney (DOE/PI); Felipe Vargas-Villamil (WVU); Doug Straub (DOE/PI); Askar Fahr (RDS)
  - Sensing and Control Strategies for Chemical Looping Coal Combustion
    - Steve Zitney (DOE/PI); Bruce Krogh (CMU); Jovan Ilic (CMU); Balaji Sukumar (CMU); Erik Ydstie (CMU)
  - Laboratory-Scale Chemical Looping Coal Combustor
    - Doug Straub (DOE/PI); Joe Mei (DOE); Josh Dalton (REM)

Overview

- **NETL/ORD CLCC Program Objectives**
  - Detailed Analysis of Oxygen Carriers for CLCC
    - Carrier performance for solid fuels
      - Experimental protocol for extracting kinetics information for oxidation of solid fuels with solid oxidant
    - Effect of S, contaminants, attrition
      - Effects on kinetics, lifespan, physical characteristics of carrier
    - Novel carrier development and analysis
  - Develop Validated Modeling Tools for Analyzing Chemical Looping Coal Combustion Components and Systems
    - CFD tools for process components
      - Individual and coupled Air and Fuel Reactors
      - Include detailed kinetics for carrier and fuel
      - CFD design platform for air and fuel reactors
    - Solid Oxygen Carrier Kinetics software
      - Software module for incorporating oxygen carrier kinetics into computational codes
    - Process Simulation – steady state and dynamic
      - Aspen Plus and NETL APECS Steady State process models
      - Develop computational platform for performance and economic evaluation of the CLCC process
      - Dynamic Simulator “Test Bed” for CLCC control strategies

Overview

- **NETL/ORD CLCC Program Objectives**
  - Develop Novel Control Algorithms for CLCC Process
    - Model-based sensing and control architectures and algorithms for CLCC systems
  - Develop Lab-Scale Chemical Looping Combustion Test Facility
    - Cold flow and reacting systems
      - Demonstrate coupled operation of air/fuel reactors
      - Demonstrate separation, recycle, and removal of carrier, ash,char
    - Validation data for Modeling Tools
    - Oxygen Carrier test facility
  - Develop NETL Design(s) for Fuel Reactor and Air Reactor
    - Developed for selected fuel and carrier particles
    - Developed based on the kinetics information extracted and fine-tuned with CFD simulations
    - Developed using small-scale physical experiments and scaled up using CFD tools
  - NETL Process Designs for New Construction and Retrofit
    - Design based on bench scale testing, CFD studies, process simulations, and control studies

Chemical Looping Coal Combustion (CLCC)

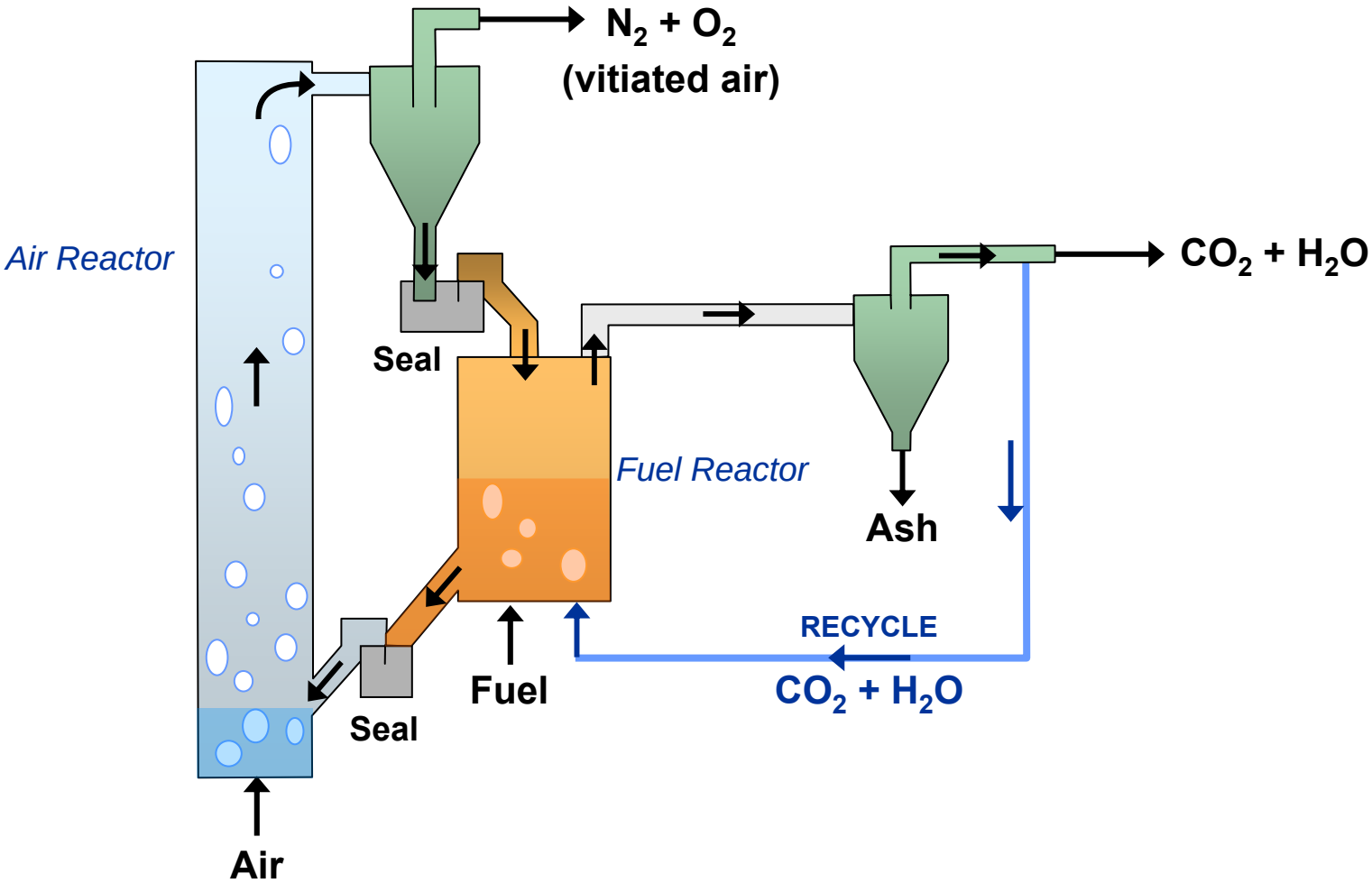
- **CLCC uses a solid metal oxide carrier to transfer oxygen from the air to fuel**
  - Separate air and fuel reactors
  - Coal Oxy-combustion

- **Direct contact between fuel and combustion air is avoided**
  - No nitrogen dilution – CO_2 and H_2O are combustion products facilitating CO_2 separation

- **Advantages of the CLCC process:**
  - Oxy-combustion of coal with no ASU required
  - Significant cost saving eliminating ASU capital and operating costs allowing process to meet COE goals of < 35%
  - Potential for 100% CO_2 capture to meet goal of > 90% capture

- **Challenges for the CLCC process with metal oxides**
  - Solids Handling
  - Complete conversion of coal
  - Separation of metal oxide carrier-char-ash
  - Thermal management between air and fuel reactors

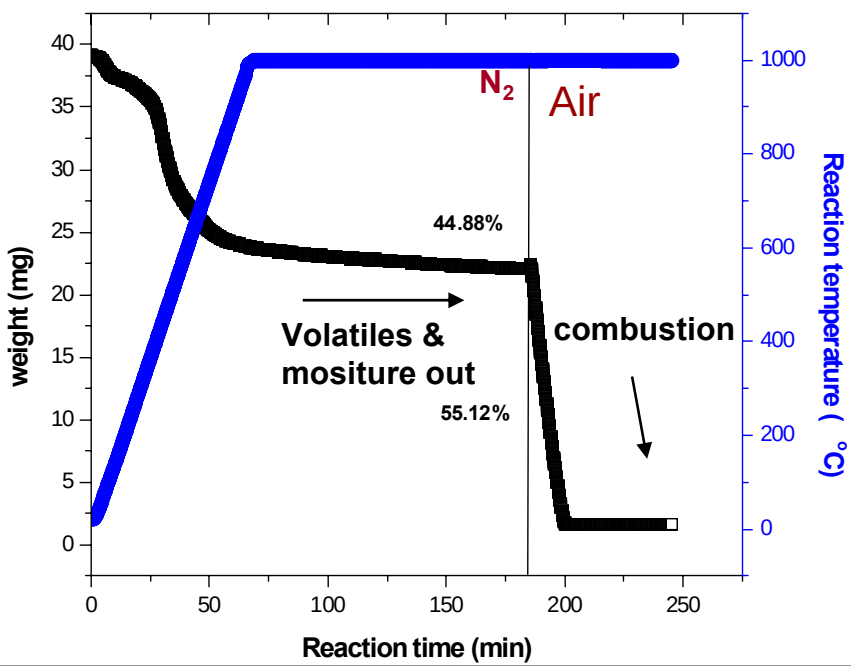
Chemical Looping Coal Combustion Process



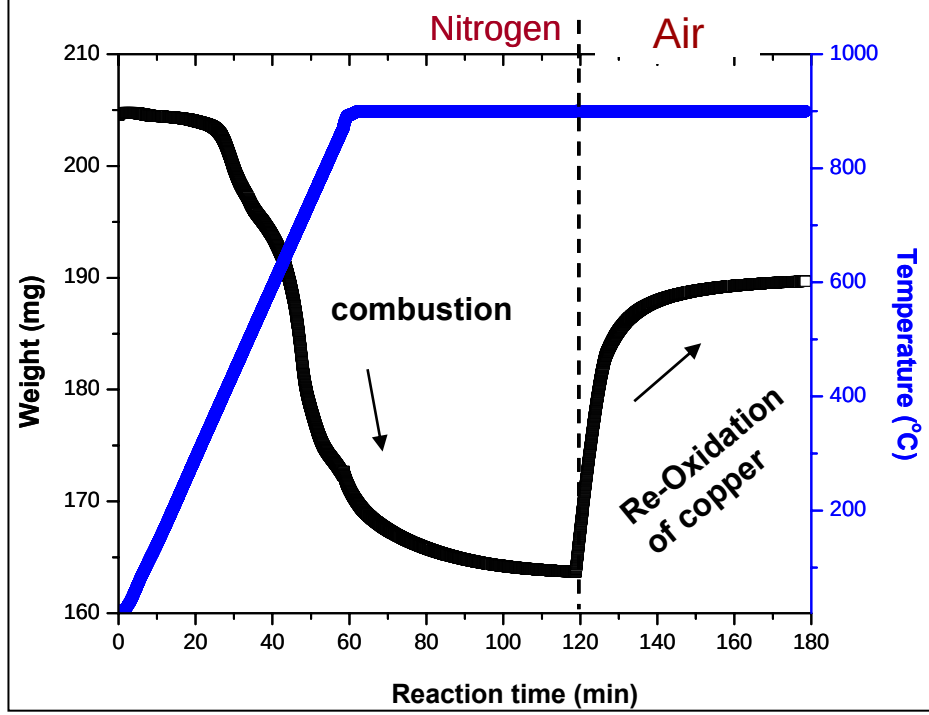
Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal

- **Progress and Current Status**
  - TGA Baseline experiments
    - Comparison of heating/combustion of coal to CLCC with CuO

TGA Profile of Coal in N_2/Air



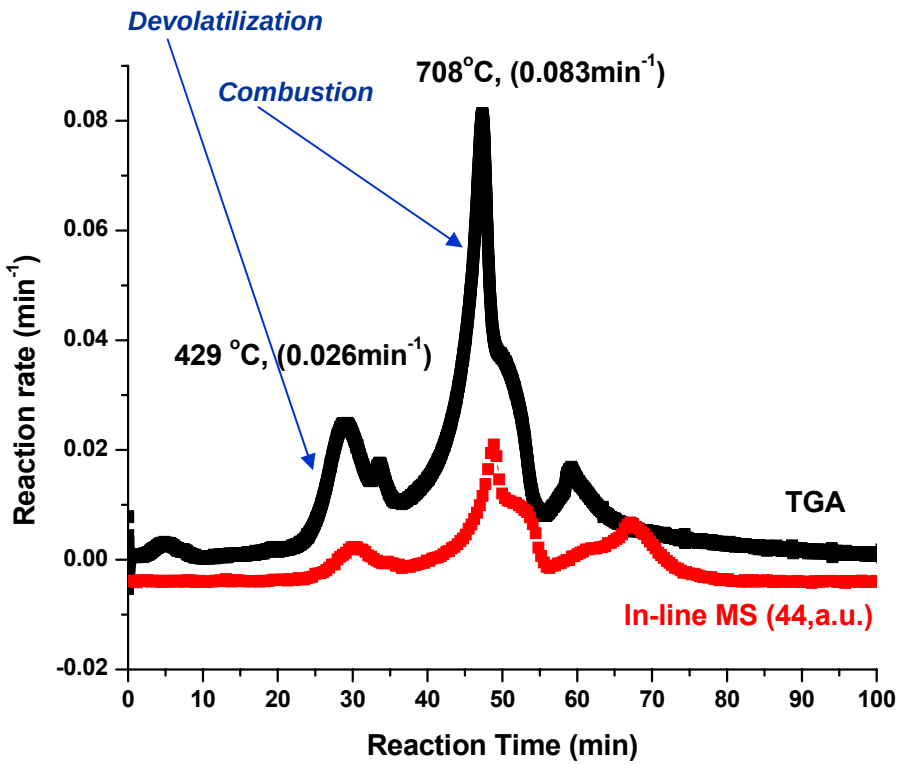
TGA Profile of Coal +CuO in N_2/Air



Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal

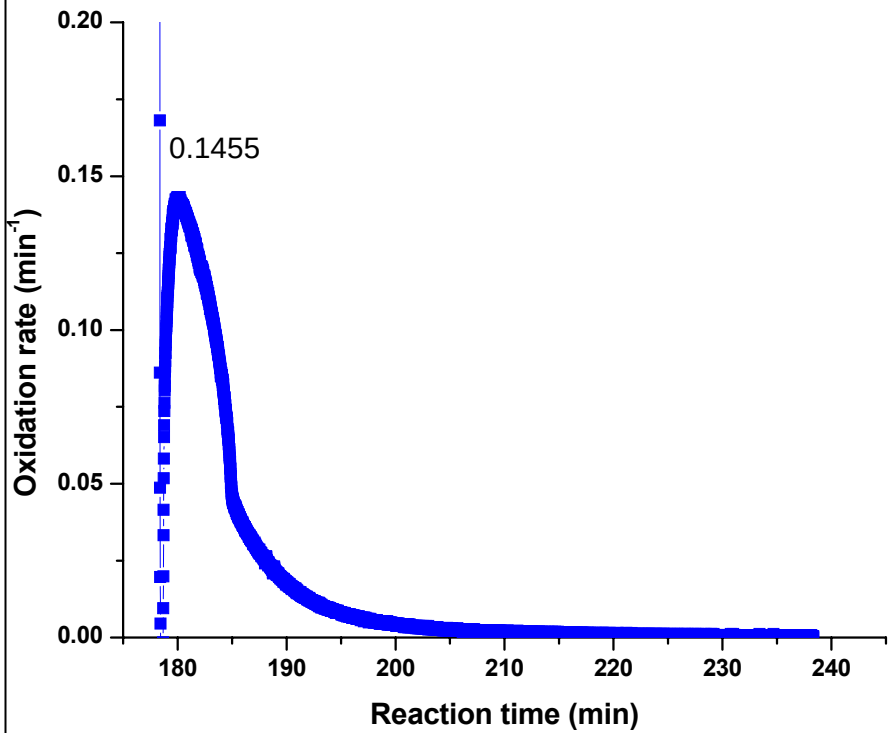
•Progress and Current Status

– Reduction Rate of Coal+CuO in N_2



- Major reaction happens at ~700 °C
- CO_2 observed from on-line MS matches TGA profiles
- No CO detected

- Oxidation Rate of CuO in Air at 900C



- Oxidation faster than combustion

Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal

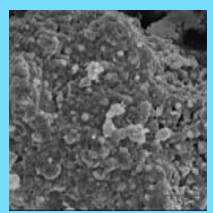
- **Progress and Current Status**
  - CLC of Coal with various metal oxides

samples	gas media	Combustion				Oxidation at 900-1000 C		
		Comb. Temp. (°C)	Comb. Rate (min^{-1})	% combustion	ΔH (kJ/mol)	Oxi. Rate (min^{-1})	oxygen uptake (%)	ΔH (kJ/mol)
CuO	CO_2	703	0.098	100	-96.5	0.172	98.6	-156
	N_2	708	0.083	100		0.175	99.2	
NiO	CO_2	993	0.061	73.05	75.2	0.84	77.5	-327.7
	N_2	1000	0.017	68.4		0.82	71.6	
Fe_2O_3	CO_2	973	0.055	94.9	79.2	0.77	93.7 Fe(II)	-347.4
	N_2	977	0.05	91.6		0.78	90.6 Fe(II)	
Mn_2O_3	CO_2	905	0.011	76.76	-36.1	0.42	72.2Mn(II)	-216.4
	N_2	978	0.01	71		0.38	68.3 Mn(II)	
Co_3O_4	CO_2	781	0.096	83.3	-8.6	1.74	78.2 Co(II)	-243.9
	N_2	781	0.096	83		1.74	78.0 Co(II)	

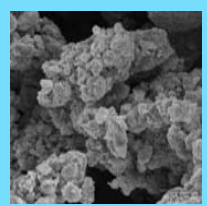
Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal

- **Progress and Current Status**
  - Summary
    - Combustion of coal feasible with metal oxides
      - Metal oxides could supply oxygen for direct coal combustion
      - Excellent combustion performance in the presence of nitrogen and CO
      - Produce sequestration ready-CO_2 by recycling CO_2 in fuel reactor
    - Reduced metal could be easily re-oxidized to metal oxide and the oxidation rate is faster than the reduction rate
    - TGA and bench scale reactor tests showed that
      - CuO has excellent reduction/oxidation performance
      - Potential oxygen carrier for solid-CLC
    - Carbon dioxide can promote the combustion reaction for some metal oxides

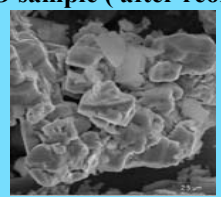
Pure CuO



Coal and CuO mixture



CuO sample (after reoxidation)



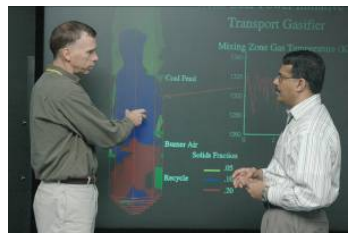
Smoother surface after reoxidation observed on CuO particles after bench scale tests at 800 °C

Evaluation of Metal Oxide Oxygen Carriers for Chemical Looping Combustion of Coal

- **Future Activities**
  - Detailed analyses of other carriers
    - Fe-based carriers of interest
  - Develop chemical kinetics models for CFD application
    - Carrier oxidation and reduction
  - Effect of coal contaminants and ash on carrier performance
  - Novel carrier development

CFD Modeling of Chemical Looping Coal Combustion

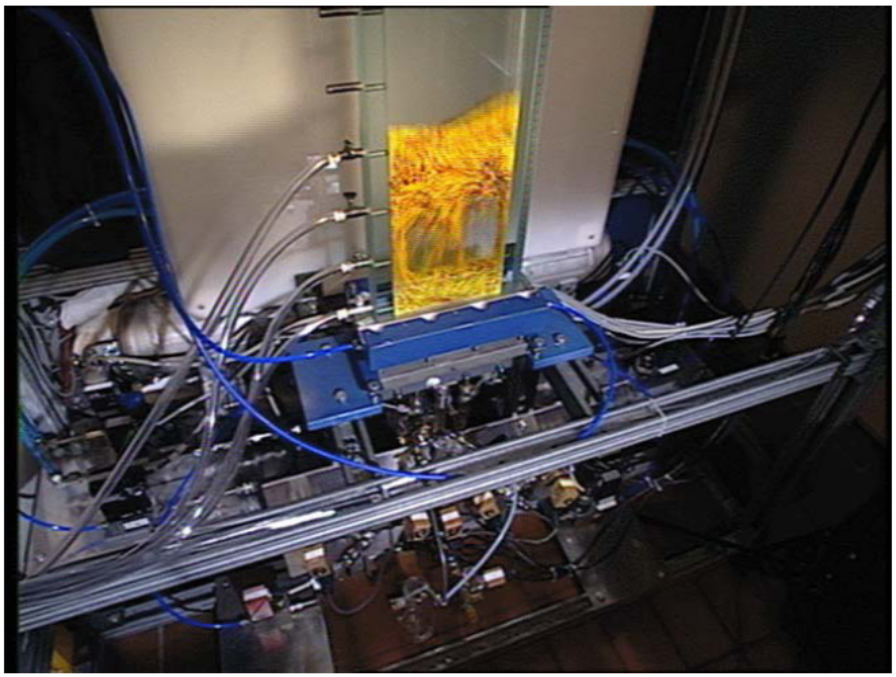
- **Goals**
  - Develop CFD models for the design and scale-up of CL reactors
  - Use simulations to investigate solutions to CL technical challenges
    - Ash-carrier separation
    - Char oxidation
    - Thermal management
    - Scale-up

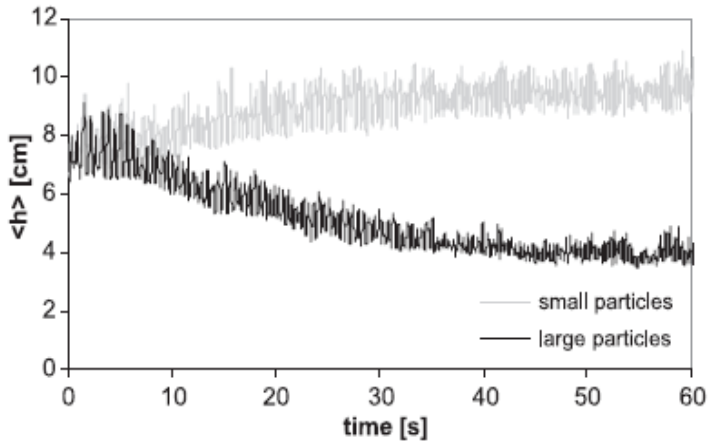


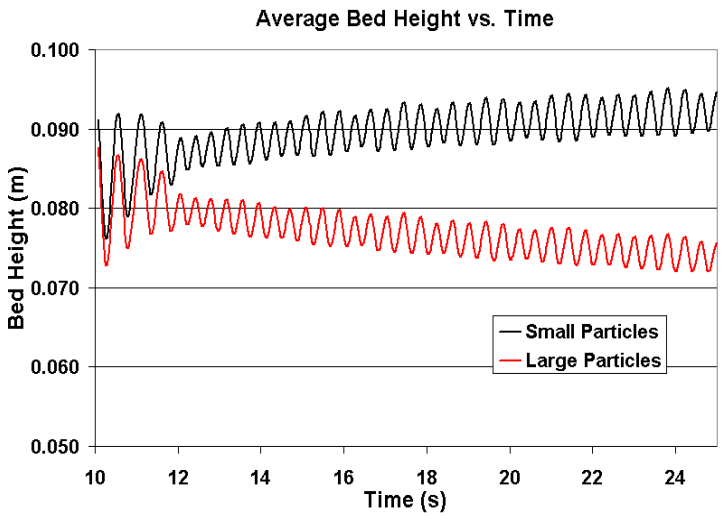
- **Technical Objectives**
  - Develop reacting flow models of air and fuel reactor
    - Incorporate chemical kinetic models using data from NETL
    - Model coupled operation of air and fuel reactors
    - Demonstrate ability to model ash-carrier separation
  - Validate models with data from NETL/ORD, other NETL contractors, literature

CFD Modeling of Chemical Looping Coal Combustion

- **Progress and Current Status**
  - Cold Flow, particle segregation simulation
    - Air, 0.95 – 1.3 m/s
    - 15x70x1.5 cm
    - 1.5 & 2.5 mm glass beads, 2523 kg/m3
    - Bed height, 7.5 – 30 cm
    - Separation under-predicted



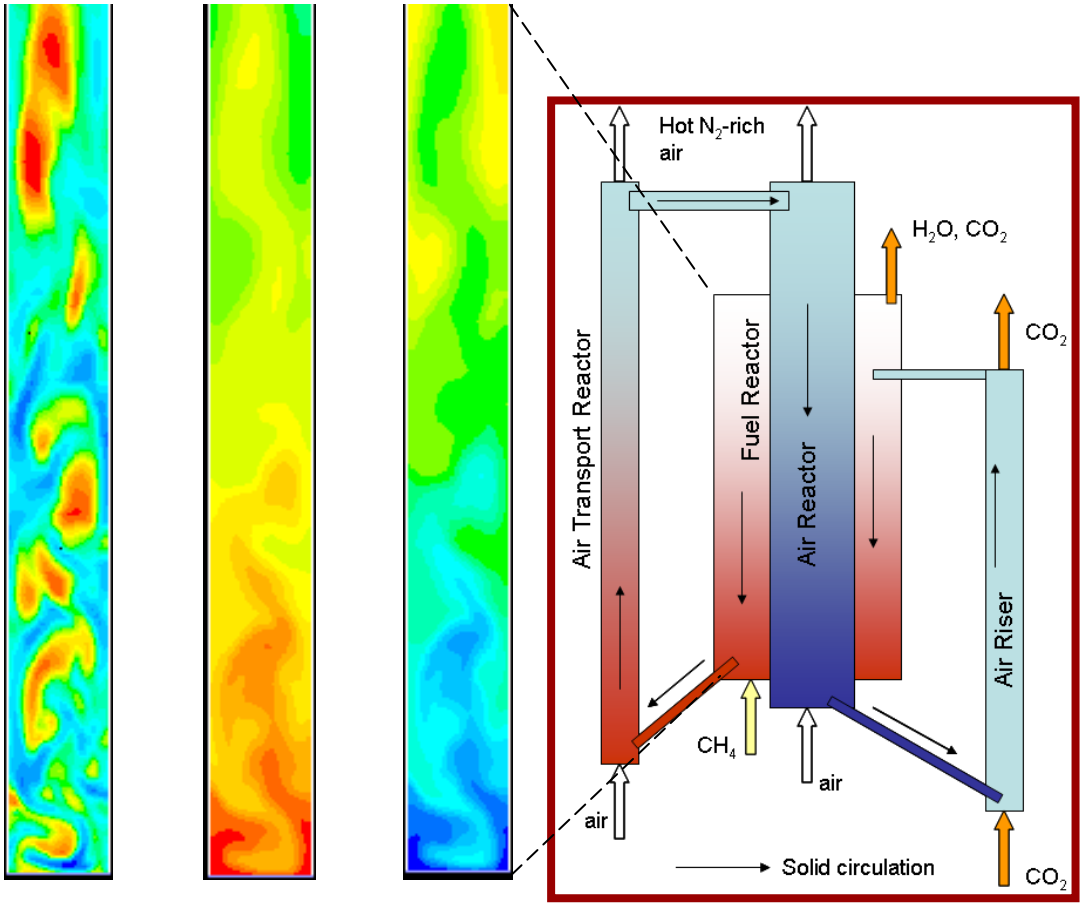




Goldschmidt, Link, Mellema, Kuipers, Powder Tech., 2003

CFD Modeling of Chemical Looping Coal Combustion

- **Progress and Current Status**
  - Gaseous Fuel CLC Simulations – Methane Combustion



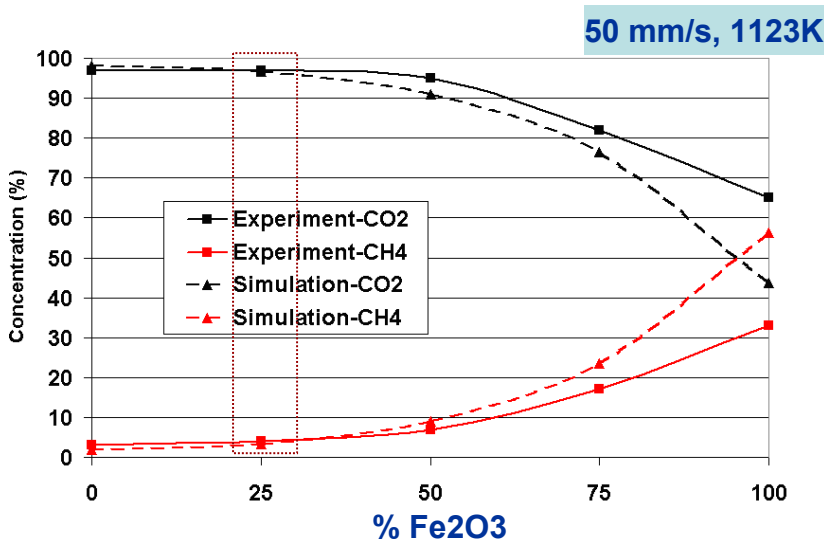
Gas vol% (50-100)	CH_4 wt%. (0-100)	CO_2 wt% (0-25)

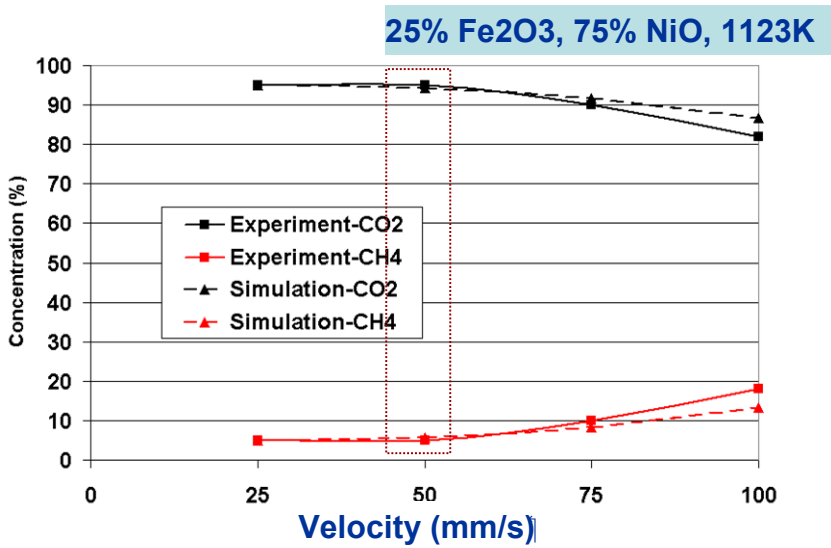
Experimental Parameters	
CH_4	25 – 100 mm/s (1-4 U_{mf})
CO_2/Air	1.5 m/s
Solids	0.8 kg, 13 kg/m_2/s
Carrier	NiO, Fe_2O_3 and bentonite (wt 40%)
Fuel Reactor	0.9 m x 55 mm
Air Reactor	1.5 m x 23 mm

Son and Kim, Ind. Eng. Res., 2006

CFD Modeling of Chemical Looping Coal Combustion

- **Progress and Current Status**
  - Gaseous Fuel CLC Simulations – Methane Combustion





- **Over-predicts fuel consumption at higher velocity**
- **Under-predicts fuel consumption at higher Fe_2O_3 fraction**
- **Approaches to reduce the discrepancy with the experiments:**
  - separate kinetic rates for each carrier species
  - add steam reforming reaction (CO production)
  - include pore and film diffusion into rate model
  - alternatives to shrinking core (deactivation, grain, etc.)

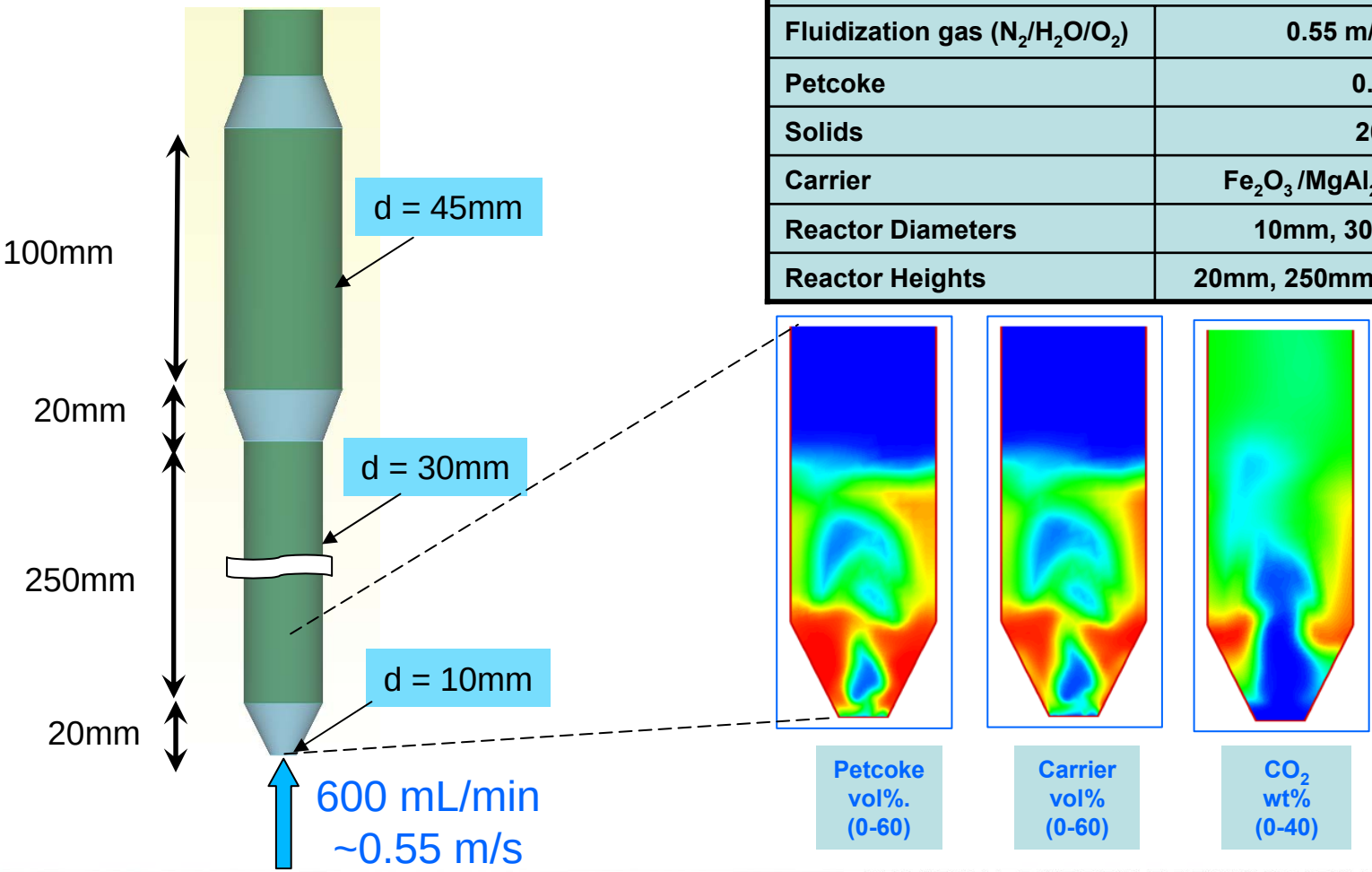
Son and Kim, Ind. Eng. Res., 2006

CFD Modeling of Chemical Looping Coal Combustion

- **Progress and Current Status**
  - Solid Fuel CLC Simulations
  - Petcoke Gasification/Combustion

Leion, Mattisson, and Lyngfelt, Fuel, 2007

Experimental Parameters	
Fluidization gas ($N_2/H_2O/O_2$)	0.55 m/s, 50 u_{mf}
Petcoke	0.2 g
Solids	20 g
Carrier	$Fe_2O_3/MgAl_2O_4$ 60/40 wt%
Reactor Diameters	10mm, 30mm, 45mm
Reactor Heights	20mm, 250mm, 20mm, 100mm



CFD Modeling of Chemical Looping Coal Combustion

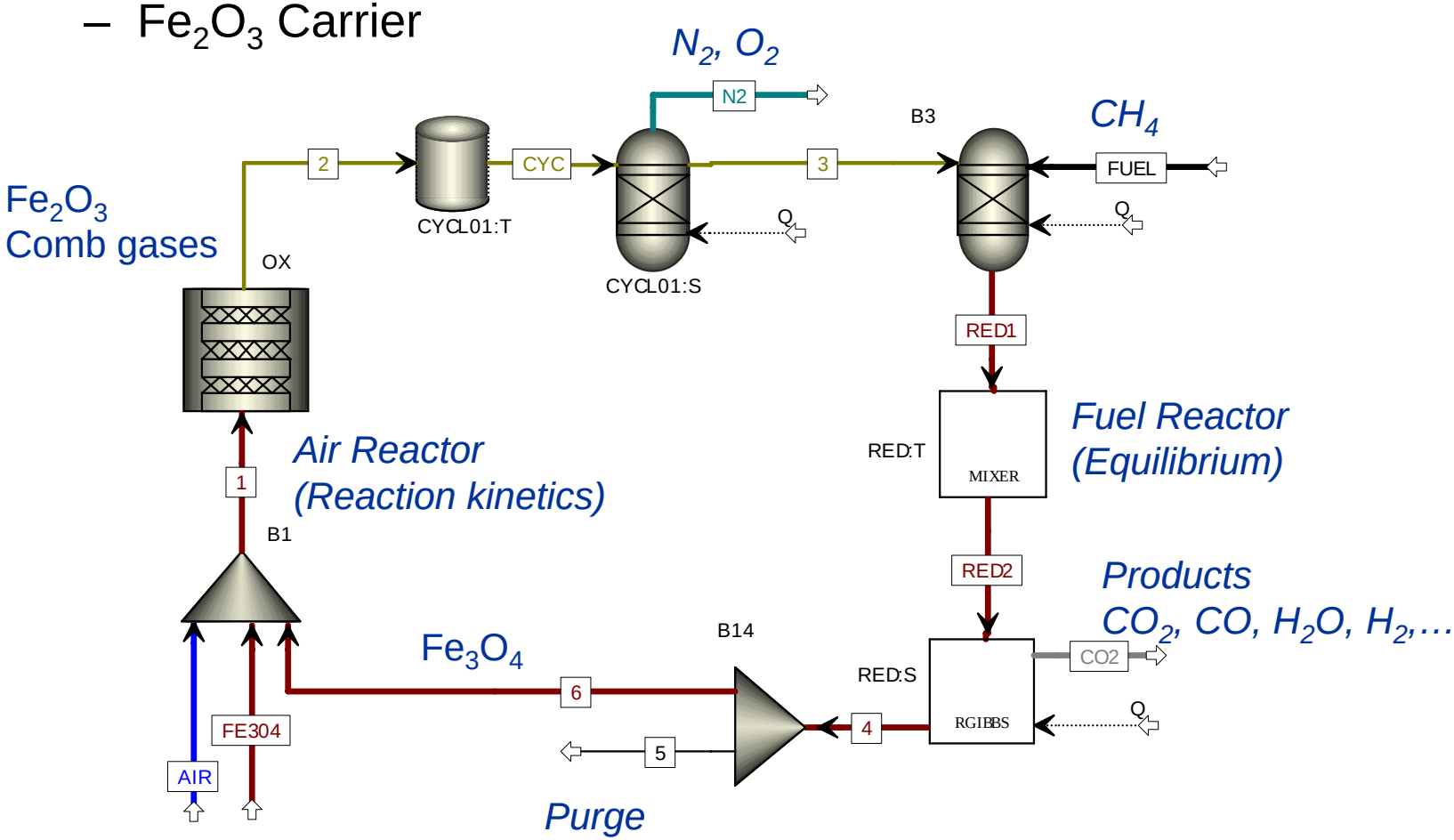
- **Future Activities**
  - Complete development and validation of fuel reactor model
    - Incorporate chemical kinetic data from NETL/ORD
  - Develop and validate air reactor model
    - Incorporate chemical kinetic data from NETL/ORD
  - Validate particle segregation model
  - Develop and validate model of coupled air and fuel reactors
  - Use CFD models for Scale-up calculations

Chemical Looping Process Simulation

- **Goals**
  - Develop plant-wide steady-state/dynamic simulations of CLCC power generation systems with carbon management
  - Optimize process design, operation, and control with respect to economic, energy, and environmental objectives
- **Technical Objectives**
  - Develop steady-state simulation of a chemical looping coal combustion system (Aspen Plus)
    - Incorporate CO_2 management system (compression, recirculation, etc.)
    - Develop economic model to determine COE from plant parameters
  - Develop CLCC dynamic simulation (Aspen Dynamics)
    - Implement low-level PID control loops
    - Analyze plant operability and controllability
  - Develop more rigorous PDE-based steady-state/dynamic models for chemical looping reactors (Aspen Custom Modeler)
  - Make use of high-fidelity CFD models (FLUENT) and ROMs in plant-wide CLCC simulations (APECS)

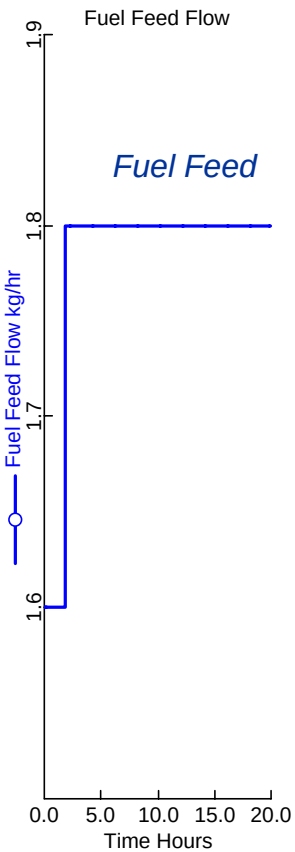
Chemical Looping Process Simulation

- **Progress and Current Status**
  - Simplified steady-state and dynamic model for CLC of CH_4
  - Fe_2O_3 Carrier

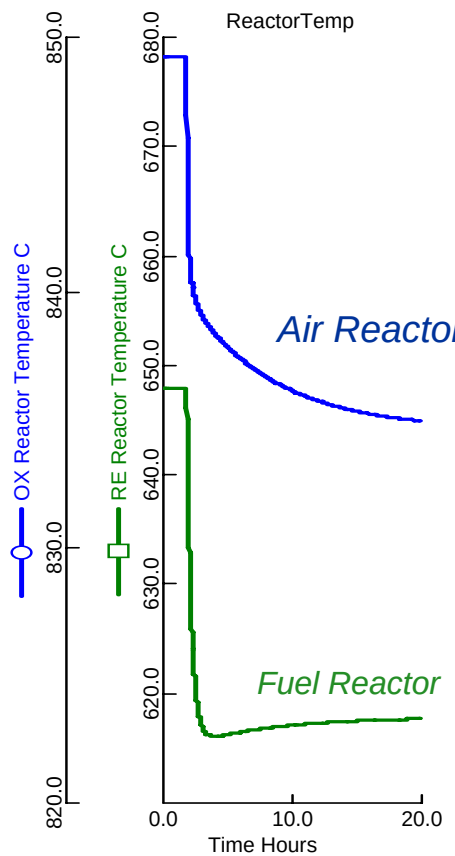


Chemical Looping Process Simulation

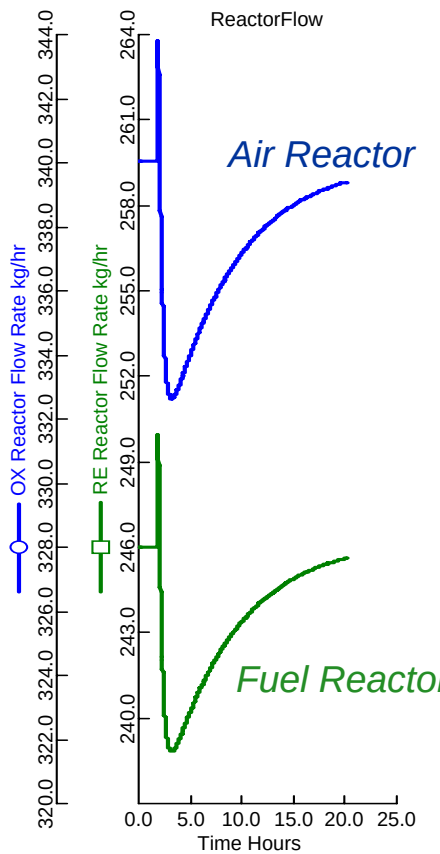
- **Progress and Current Status**
  - Open-Loop Dynamics
    - e.g. Small fuel feed step increase



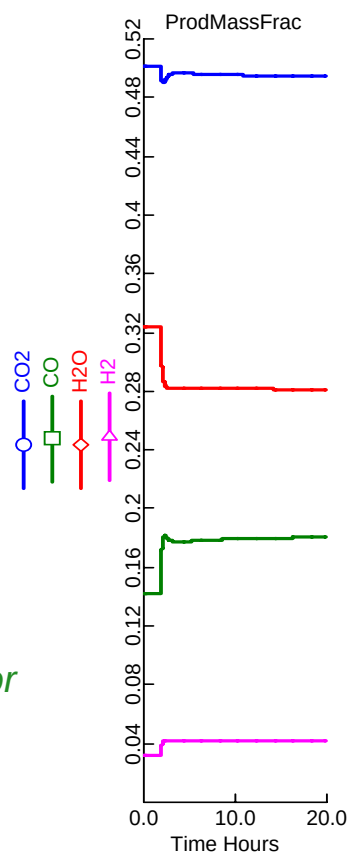
Fuel Flow



Reactor Temperature



Reactor Flow



Fuel Reactor Products

Chemical Looping Process Simulation

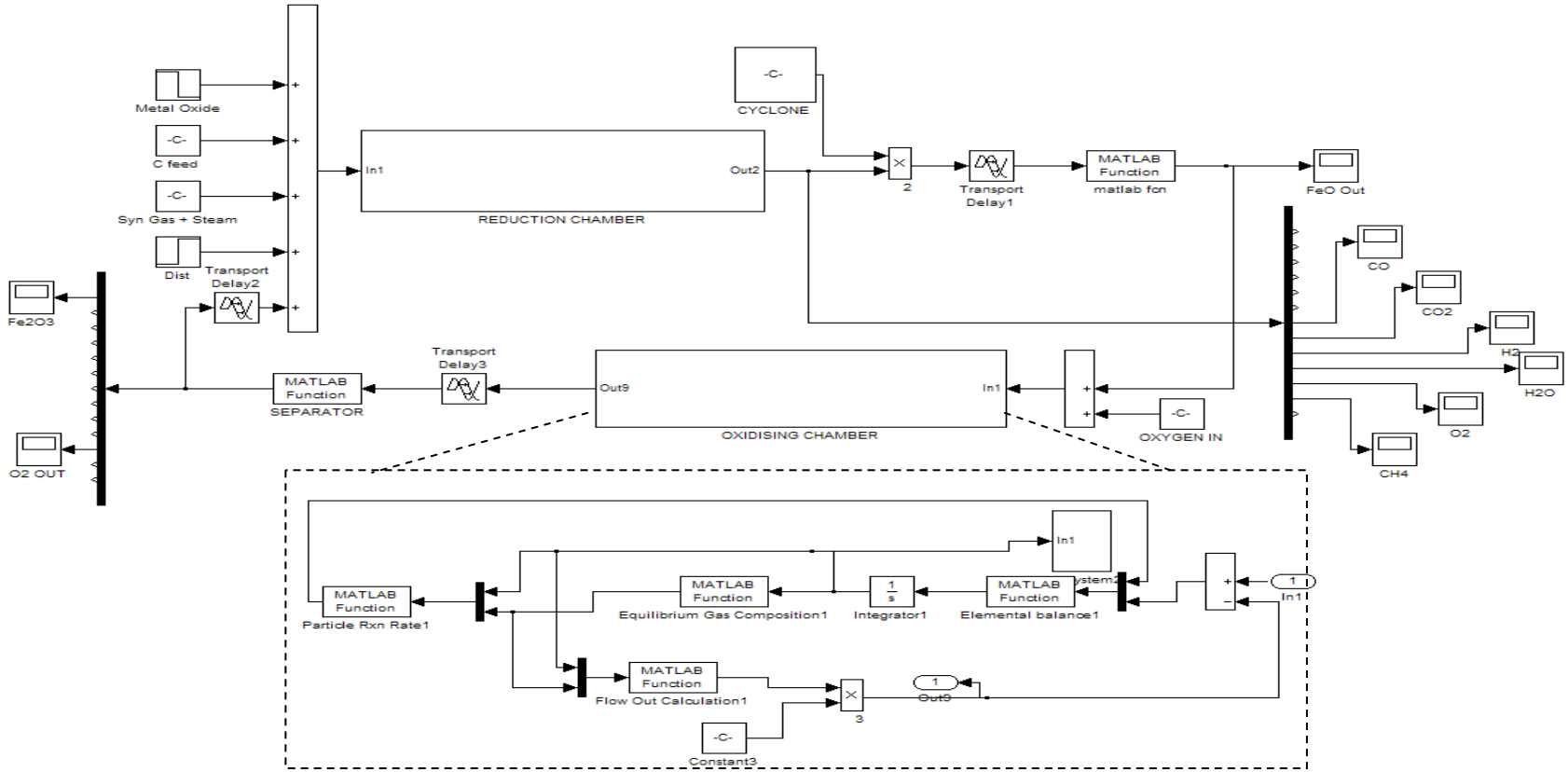
- **Future Activities**
  - Develop Steady-State Aspen Plus model of Fe- and Cu-based CLCC process
    - Include CO_2 management system
  - Develop dynamic Aspen Dynamics model of Fe- and Cu-based CLCC process
    - Include CO_2 management system
    - Implement control loops
  - Develop economic model based on process simulations to evaluate plant COE

Sensing and Control Strategies for Chemical Looping Combustion

- **Goals**
  - Develop flexible and extensible model-based sensing and control architectures and algorithms for CLCC systems
- **Technical Objectives**
  - Develop dynamic simulation and control-oriented models of CLCC systems, including the manipulated variables, disturbances, and possible measured variables
  - Formulate real-time sensing and control problem for CLCC systems
  - Determine appropriate sensing strategies, possibly including new sensing technologies being developed by NETL
  - Develop signal processing and control algorithms to optimize process performance subject to multiple operating objectives and constraints
  - Implement and experimentally demonstrate/evaluate a complete real-time control system, incorporating new sensors and covering a full range of expected operating conditions

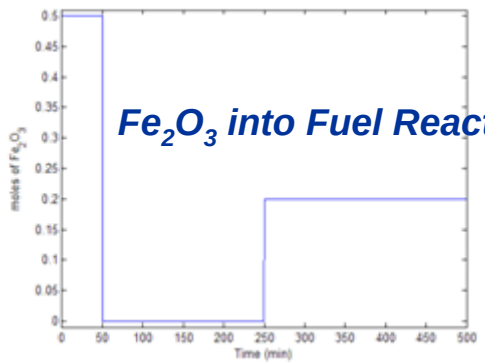
Sensing and Control Strategies for Chemical Looping Combustion

- **Progress and Current Status**
  - Developed Simulink model of coupled air/fuel reactors
    - Simplified – fuel is syngas; carrier is Fe_2O_3
    - Elemental Balance – gas phase, equilibrium assumption
    - Population balance – solids phase
    - Shrinking core mechanism for solid carrier

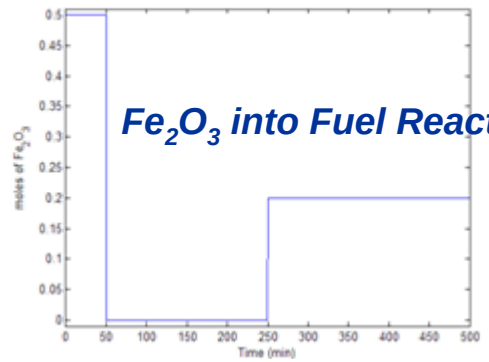


Sensing and Control Strategies for Chemical Looping Combustion

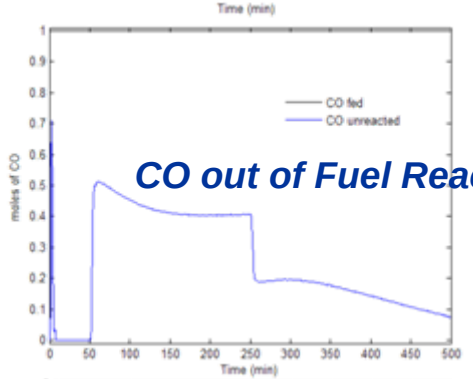
- **Progress and Current Status**
  - Preliminary model results for variation in carrier flow



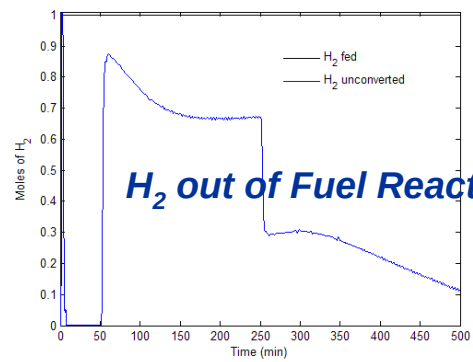
Fe_2O_3 into Fuel Reactor



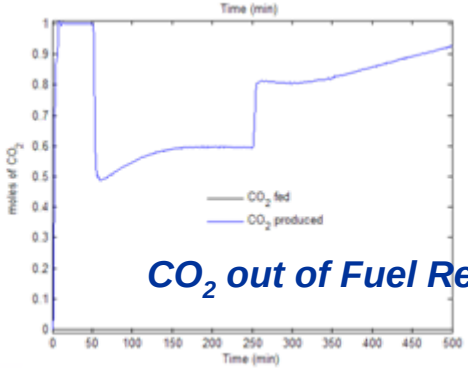
Fe_2O_3 into Fuel Reactor



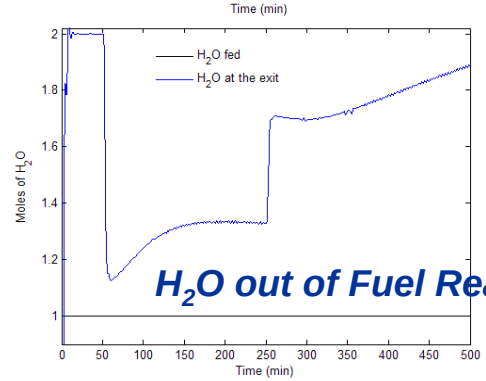
CO out of Fuel Reactor



H_2 out of Fuel Reactor



CO_2 out of Fuel Reactor



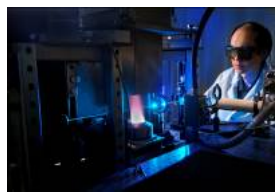
H_2O out of Fuel Reactor

- **Future Activities**
  - Upgrade Simulink model for coal fuel
    - Validate model with NETL and literature data
  - Evaluate novel sensing strategies
  - Evaluate use of model-based control

Laboratory-Scale Chemical Looping Coal Combustor

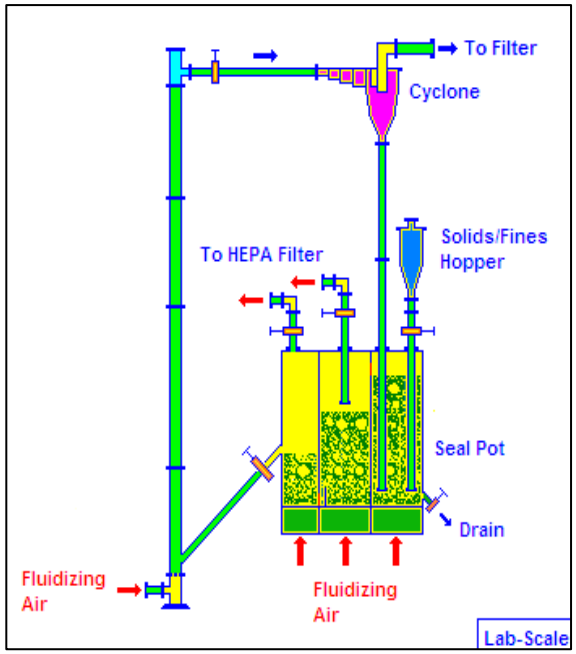
- **Goals**
  - Develop a Bench-Scale NETL chemical looping coal combustor facility
    - Includes cold flow and reacting flow capability
    - Coupled operation of air and fuel reactors
    - coordinated with other efforts in modeling chemical looping
  - Provide detailed data for model validation
  - Provide test bed for carrier performance evaluation

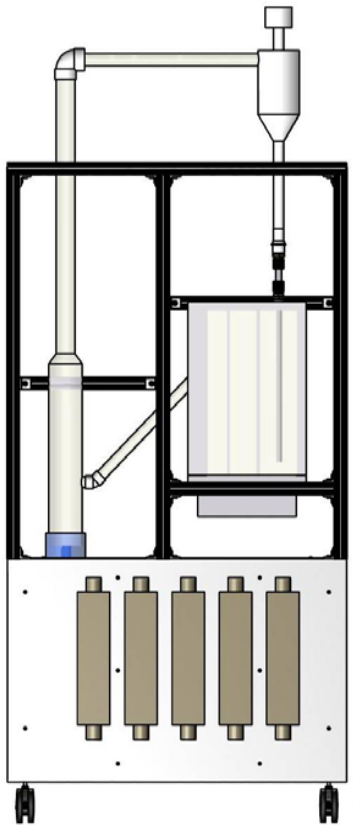
- **Technical Objectives**
  - Design and construction of cold flow facility
    - Detailed data for CFD model validation
  - Design and construction of hot flow facility
    - Detailed data for CFD model validation
    - Dynamic data for dynamic process model validation
    - Extended tests of carrier performance

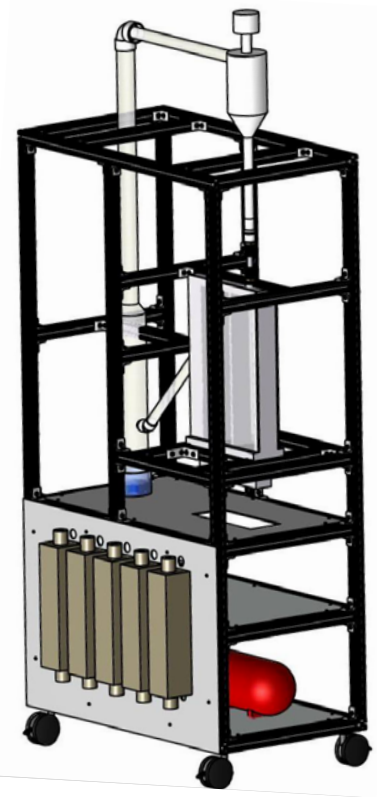


Laboratory-Scale Chemical Looping Coal Combustor

- **Progress and Current Status**
  - Cold flow demonstration facility has been constructed
  - Cold flow system operated with air and fuel reactors coupled







Laboratory-Scale Chemical Looping Coal Combustor

- **Future Activities**
  - Complete instrumentation of cold flow unit
  - Run cold flow experimental program studying particle (ash-char-carrier) separation
    - Generate data for CFD model validation
    - Generate data for dynamic process model validation
  - Design and construct reacting flow laboratory scale CLCC system
    - Generate data for CFD model validation
    - Generate data for dynamic process model validation
    - Evaluate carrier performance at reacting flow conditions

Summary of the NETL/ORD CLCC Program

- **Evaluation of Carrier Performance**
  - Chemistry in fuel and air reactors
  - Durability
  - Ash interaction
  - Effects of coal contaminants
  - Novel Carrier Development

- **Development of Computational Tools to Support CLCC Analyses**
  - CFD tools for design and evaluation of air and fuel reactor performance
  - Steady state process models – economic analysis capability
  - Dynamic process models

- **Novel Sensor and Control Strategies for CLCC Systems**

- **Laboratory Scale Test Facility**
  - Cold flow performance
  - Reacting flow performance of coupled air and fuel reactor system

- **Balanced Research Program**
  - Support the NETL CLCC research program – external and in-house
  - Tools and Data to help design new and retrofit CLCC systems