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Development of Enabling Technologies for Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling

Project DE-FE0029160

Kevin J. Whitty
University of Utah

JoAnn S. Lighty
Boise State University

Hong-Shig Shim
Reaction Engineering International

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Project Overview

Participants: The University of Utah, Boise State University, Reaction Engineering International, CPFD Computational Particle Fluid Dynamics

Funding:

Source	U Utah	Boise State	REI	TOTAL	%
DOE	$ 1,073,687	$ 50,116	$ 210,000	$ 1,333,803	74%
Cost share	$ 268,421	$ 12,530	$ 179,250	$ 460,201	26%
TOTAL	$ 1,342,108	$ 62,646	$ 389,250	$ 1,794,004	100%

Project Dates: October 1, 2016 – September 30, 2019

Objectives: Develop technologies to improve performance and economic competitiveness of CLC and CLOU.

Project Structure

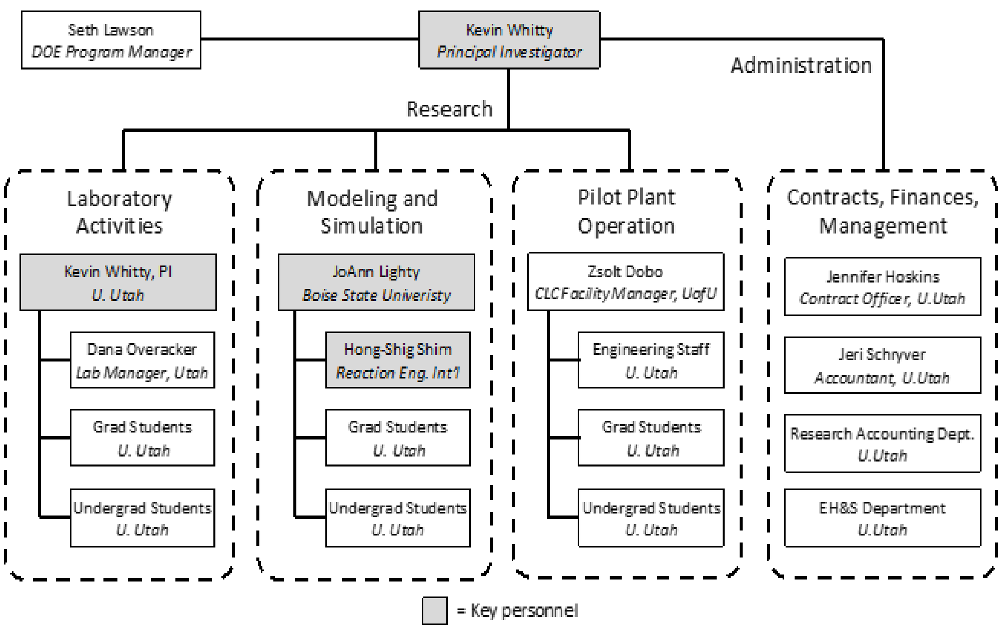
Project partners:

University of Utah
Prime recipient

Boise State University
Subcontractor

Reaction Engineering International
Subcontractor

CPFD Software
Third Party Cost Share



Project Objectives

- Primary objective: Advance development of technologies to address challenges with, and to improve performance and economics of, chemical looping combustion
- Specific objectives
  1. Evaluate technology for recovery/recycle of oxygen carrier metals
  2. Improve performance of dual bed CLC systems through better loop seal and gas-solid separator design
  3. Improve simulation of CLC systems though better implementation of gas-solid chemistry and reaction kinetics in CFD codes
  4. Improve heat management and recovery in dual-bed CLC systems
  5. Evaluate a new CLC reactor design with potential to improve CO_2 capture and fuel conversion while reducing oxygen carrier costs

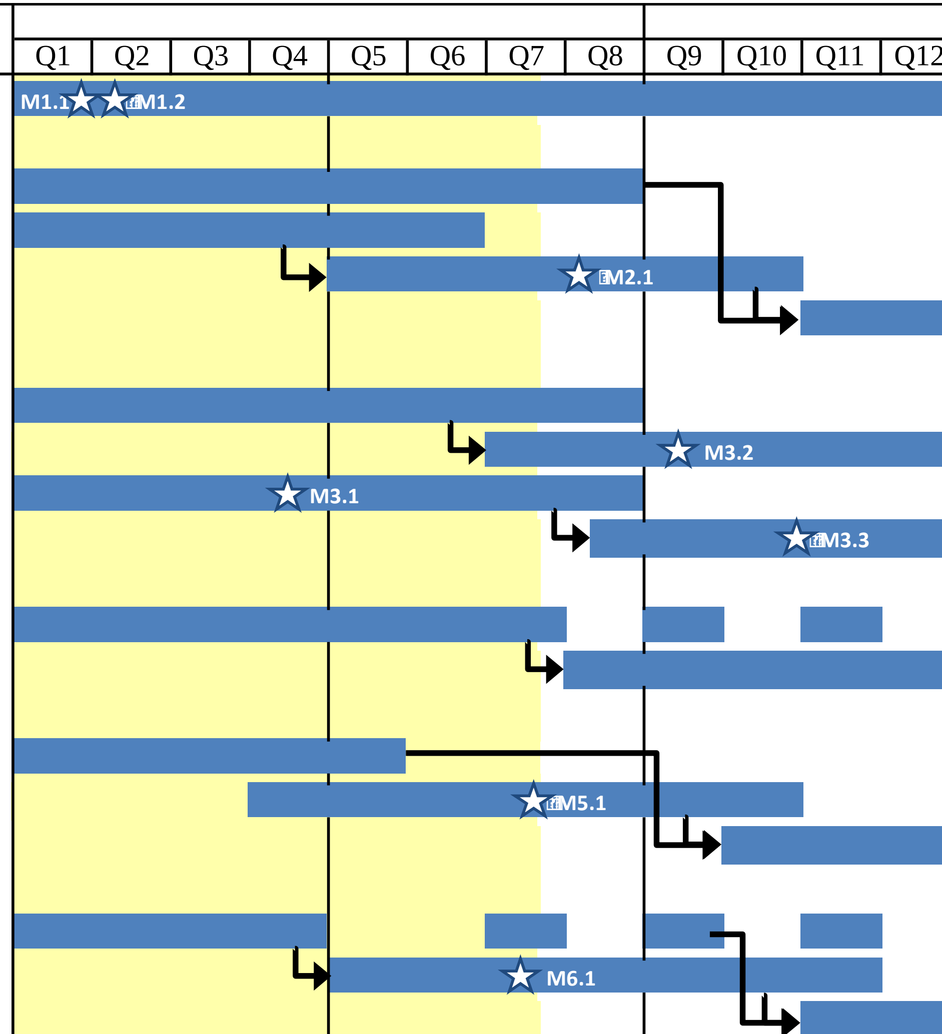
Technical Approach

- Combination of research approaches
  - Lab-scale studies
  - Pilot-scale studies
  - Reactor simulation
  - Process modeling

- Five technical tasks (plus one management task)
  1. Project management
  2. Development of "zero loss" oxygen carrier processing
  3. Improvement of solids management
     - Loop seal design
     - Gas-solid separation
  4. Implementation of chemical reactions in simulations
  5. Heat management and integration
  6. Evaluation of novel chemical looping reactor designs

Project Schedule

TASK
Task 1 - Project management and planning
Task 2 - Development of zero-loss oxygen carrier processing
2.1 - Evaluation of oxygen carrier/ash interactions
2.2 - Lab-scale studies of copper recovery from spent carriers
2.3 - Bench-scale operation of carrier recovery/recycle system
2.4 - Design of pilot oxygen carrier recovery/recycle system
Task 3 - Improvement of solids management
3.1 - Simulation and cold-flow studies of loop seal designs
3.2 - Evaluation of new loop seal designs at PDU scale
3.3 - Simulation and cold-flow of solids separation systems
3.4 - Evaluation of new solids separation system at PDU scale
Task 4 - Improved implementation of reactions in simulations
4.1 - Improve representations of chemical reactions
4.2 - Comparison of old and improved simulations
Task 5 - Heat management and integration of reactors
5.1 - Evaluation of heat balance between air and fuel reactors
5.2 - Study of in-bed heat removal in air and fuel reactors
5.3 - Design of boiler banks for industrial scale CLC
Task 6 - Evaluation of a novel chemical looping reactor design
6.1 - Simulation of 10 kW design of two-carrier CLC system
6.2 - Bench-scale testing of two-carrier fuel reactor
6.3 - Design of PDU modifications for two-carrier fuel reactor



Approach, Progress, Status

Task 2: Development of "zero loss" oxygen carrier processing

Task 3: Improvement of solids management

Task 4: Improved CLC reaction kinetics for simulations

Task 5: Heat management and integration of reactors

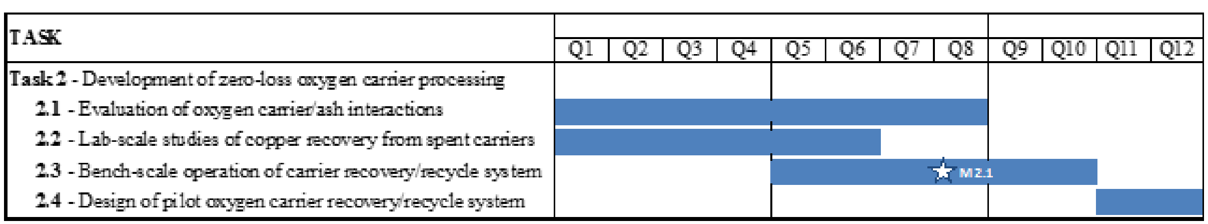
Task 6: Evaluation of novel chemical looping reactor design

Task 2:
Development of Zero-Loss Oxygen Carrier Processing

2. Development of Zero-loss Oxygen Carrier Processing

- 2.1 Evaluation of oxygen carrier/ash interactions
- 2.2 Study of copper recovery from spent oxygen carriers
- 2.3 Bench-scale operation of carrier recovery/recycle system
- 2.4 Design of pilot oxygen carrier recovery/recycle system

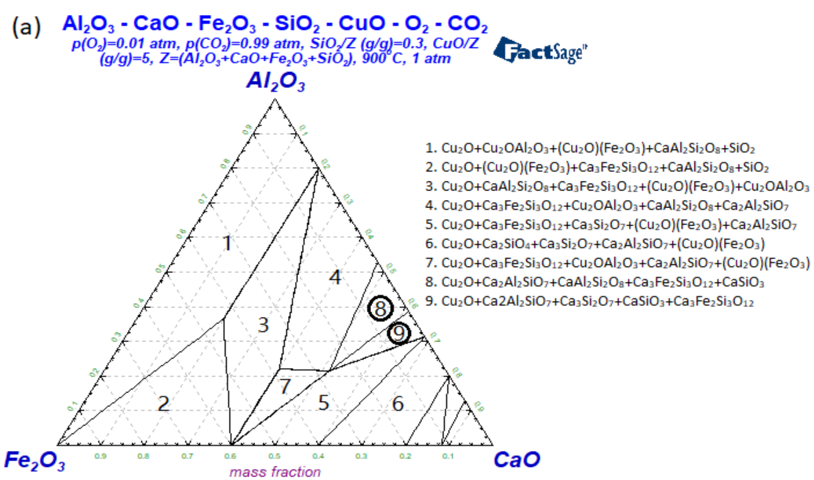
- Objective: Minimize make-up oxygen carrier requirements
- Three causes
  - Loss of activity by reactions with e.g. coal ash to form new compounds
  - Loss of activity due to agglomeration
  - Loss of material through attrition and/or carryover
- Approach
  - Modeling of solid-phase chemistry in reactor to understand risk regimes
  - Development of process to recover and recycle lost active metal (Cu)

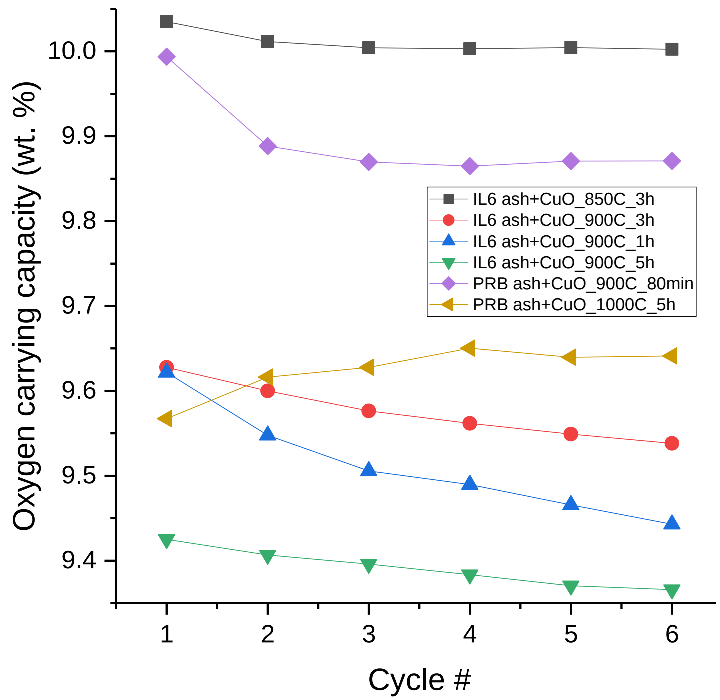


Task 2 Approach

Development of ‘Zero Loss’ Oxygen Carrier Processing

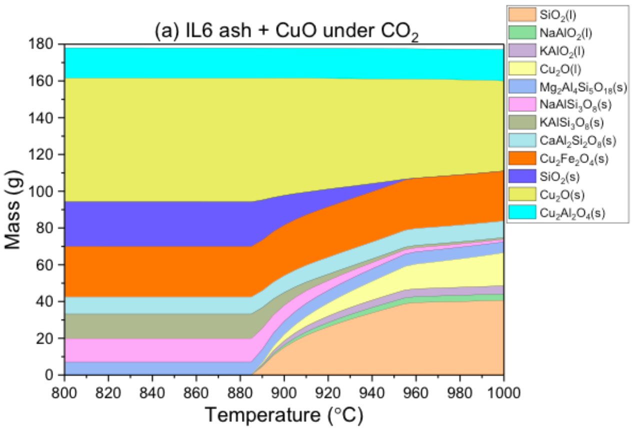
- Interactions of coal ash and oxygen carrier
  - FactSage thermodynamic modeling
    - Different mixtures of metals
    - Various gas environments
    - Temperature range 850-1000°C
  - Experimental analyses
    - TGA with mixtures of ash and Cu, Fe oxides
    - Fluidized bed tests with carrier + coal ash
    - XRD analysis to identify phases

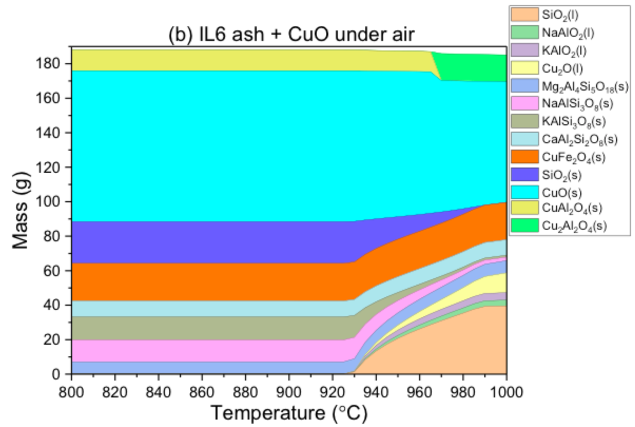


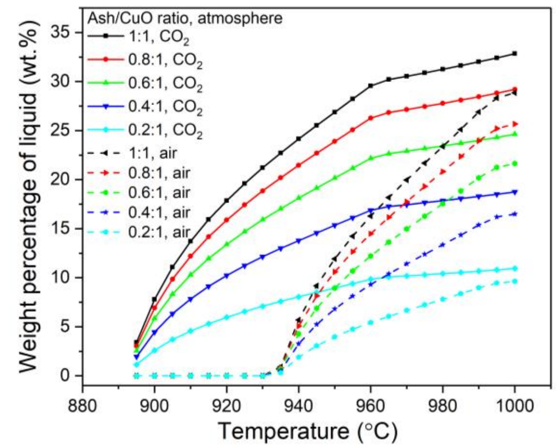


Task 2: Interaction of coal ash and copper

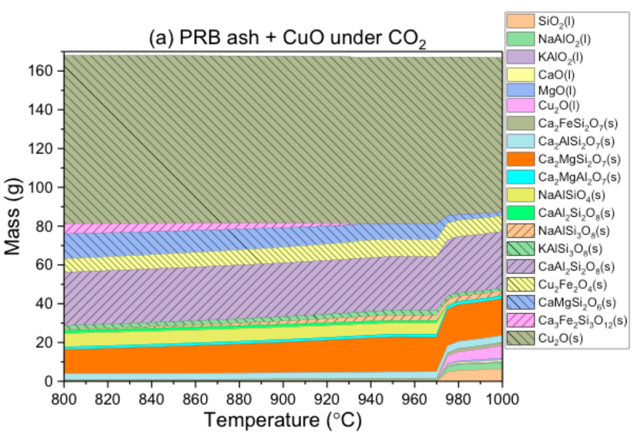
Predicted compositions of ash/CuO mixtures versus temperature

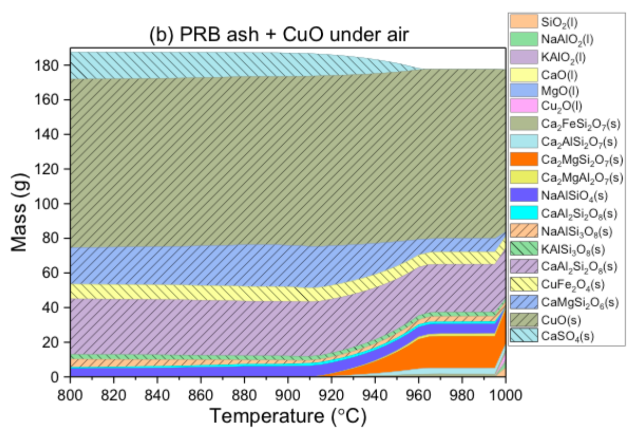


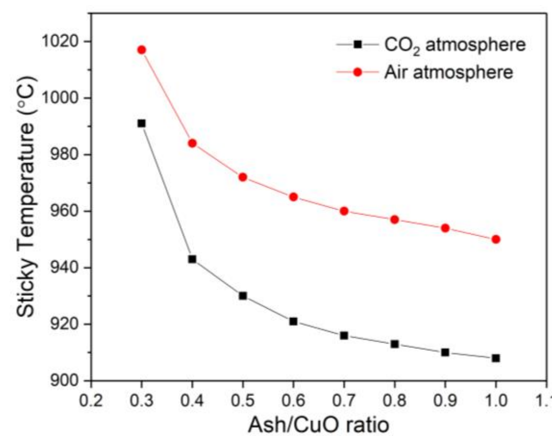




Dependence of liquid wt. % on T, IL6 ash/CuO ratio, and atmosphere.

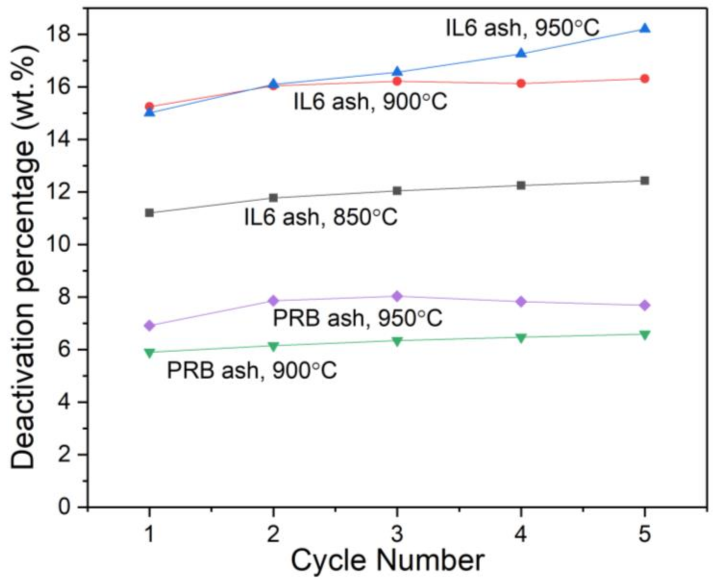




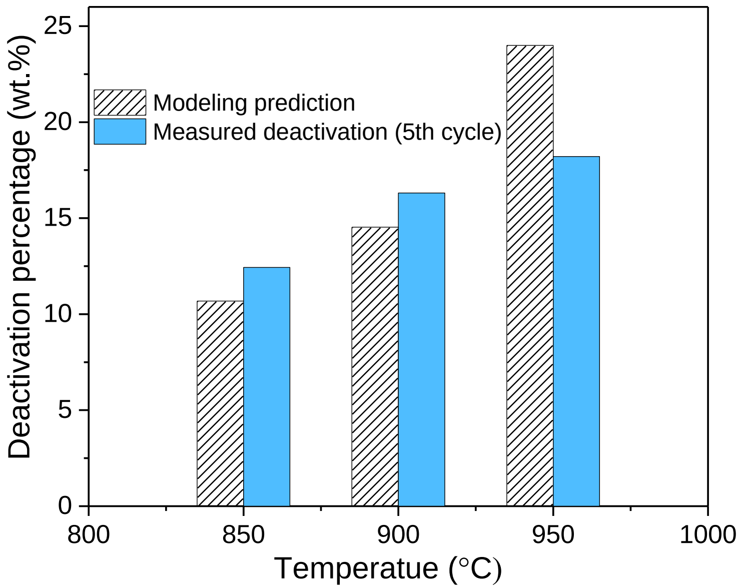


Predicted sticky temperature (T_{15}) of IL6 ash/CuO mixture.

Task 2: Interaction of coal ash and copper



Deactivation percentage of CuO in the presence of IL6 and PRB ash measured by TGA redox cycles starting with ca. 10 mg CuO and 10 mg ash.



Modeling prediction vs. measured deactivation of IL6 ash/CuO mixture with a mass ratio of 1:1.

- Significant deactivation and sintering of CuO caused by IL6 ash
- Strong surface affinity between IL6 ash and CuO
- PRB ash proved to be relatively unreactive to CuO
- Reasonable thermodynamic modeling accuracy

Task 2 Approach
Development of Zero-Loss Oxygen Carrier Processing

- **Recovery**
  - Selectively remove copper from spent carrier

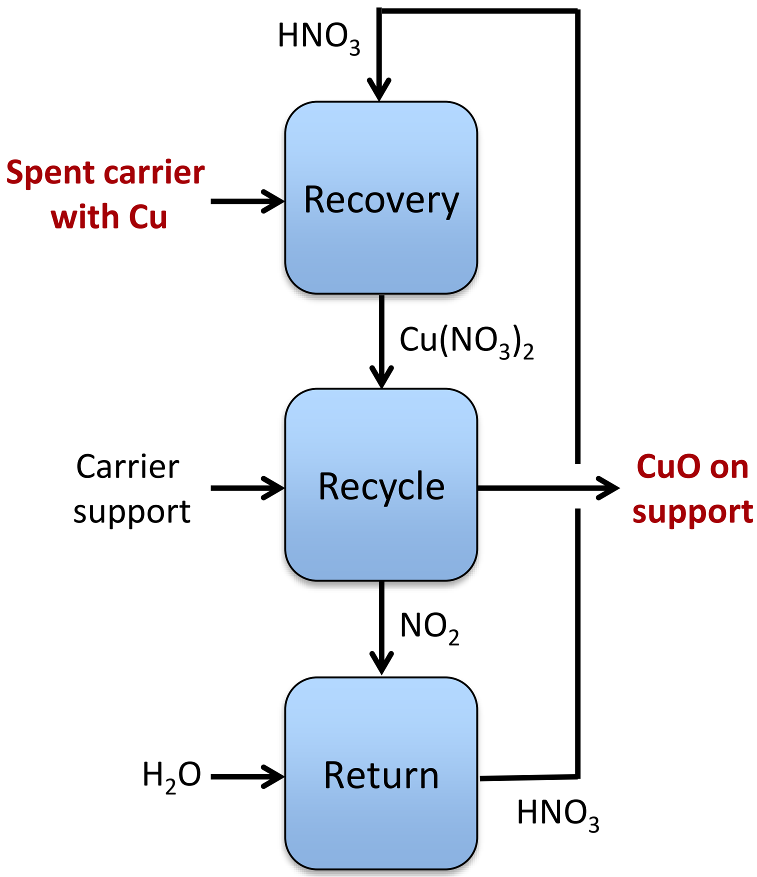
    $CuO(s) + 2\ HNO_3(aq) \rightarrow Cu(NO_3)_2\ (aq) + H_2O$

  - Baghouse will also contain coal ash/char
    - Dissolution of Cu by HNO_3 faster than coal ash
- **Recycle**
  - Recovered copper nitrate used to re-form carrier
    - Wet impregnation
    - Same technique used by UofU for carrier production
  - Calcination of impregnated carrier (180°C)

    $Cu(NO_3)_2(s) \rightarrow CuO(s) + 2\ NO_2(g) + ½O_2(g)$

- **Nitric acid / nitrate cycle**
  - Released NO_2 from calcination re-forms nitric acid

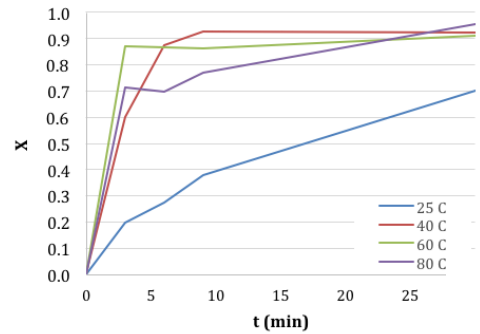
    $2\ NO_2(g) + H_2O + ½O_2(g) \rightarrow 2\ HNO_3(aq)$

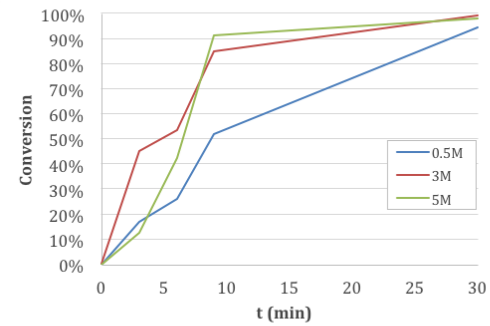


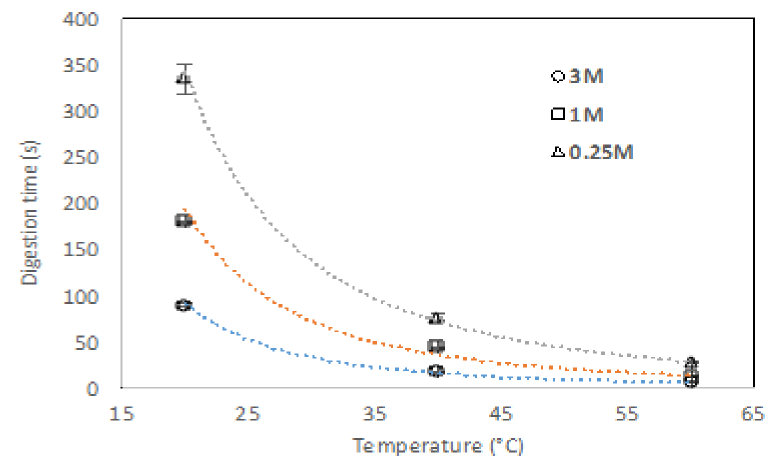
Status of Task 2:

Development of ‘Zero Loss’ Oxygen Carrier Processing

- Selective recovery of Cu from spent solids
  - Focus on PRB and Illinois #6 coals
  - Lab measurements of dissolution rates of Cu versus coal ash in nitric acid
- Results
  - Water washing step is required prior to acid dissolution
  - At all temperatures and acid strengths near complete recovery was achieved.





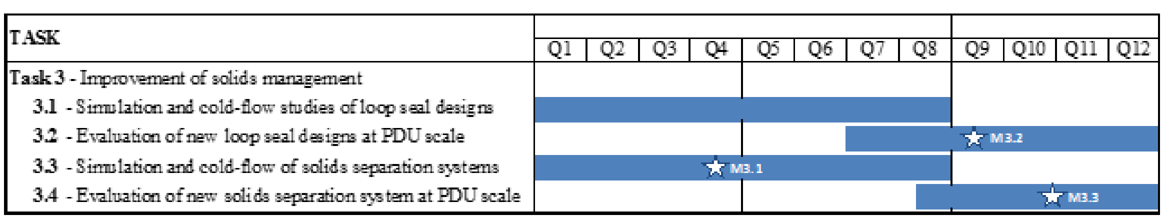


Dissolution of CuO in nitric acid

Task 3:
Improvement of Solids Management

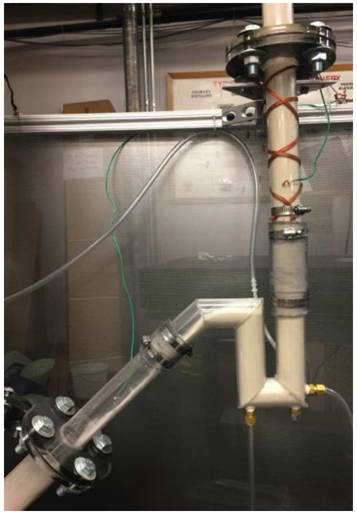
3. Improvement of Solids Management
- 3.1 Simulation and cold-flow studies of loop seal design
- 3.2 Evaluation of new loop seal designs at PDU scale
- 3.3 Simulation and cold-flow studies of solids separators
- 3.4 Evaluation of new solids separation system at PDU scale

- Objective: Improve reactor performance through better control of particle circulation and and gas-solid separation
- Two main focus areas
  - Loop seals
  - Gas-solid separators (cyclones)
- Approach
  - Simulation
  - Prototype testing
  - Evaluation on PDU



Task 3 Approach
Improvement of Solids Management

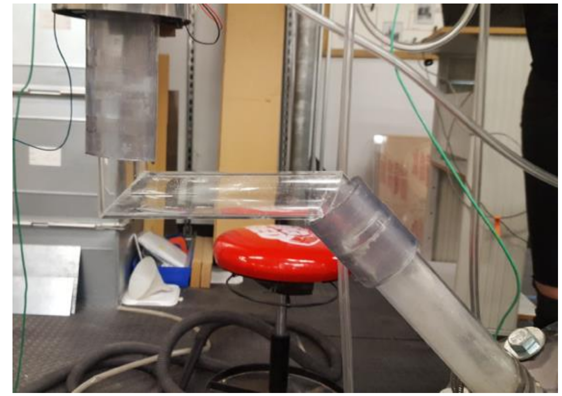
- **Loop seal design**
  - Evaluate alternate designs
    - Seal pots, L-valves, etc.
    - Try to minimize fluidizing gas requirements
  - Development process
    - Simulation in Barracuda™
    - Construct/test best designs on cold-flow model
    - Construct/test best 2-3 of those designs on PDU



- **Gas-solid separation design**
  - Evaluate alternative designs
    - Other cyclones
    - Disengagers
    - Try to get good ash/carrier particle separation
  - Development process
    - Simulation in Barracuda™
    - Construct/test best designs on cold-flow model
    - Construct/test best one of those designs on PDU

Status of Task 3:
Improvement of Solids Management

- **Loop seal design**
  - Simulations of several designs completed
  - Initial designs built in acrylic and installed on cold flow unit



L-valve simulation

Double bottom

Triple bottom

Side + bottom

Variations of gas input

Status of Task 3:
Improvement of Solids Management

- **Gas-particle separations**
  - Sensitivity analysis of simulation parameters performed for cyclones
  - Simulation of alternate separator designs
    - Cyclone geometries
    - Upflow disengager
    - Downflow disengager
- **Current focus**
  - Modified, smaller geometry disengager
  - Relies on terminal velocity for separation
  - 99+% of carrier material recovered
  - 60% of fine ash recovered

Task 4:
Improved Implementation of Reactions in Simulations

4. Improved Implementation of Reactions in Simulations

- 4.1 Improve representations of chemical reactions
- 4.2 Comparison of old and new simulations

- Accurate modeling is crucial in system scale-up effort
- Chemical reactions occurring in the system needs proper material treatment and submodel implementation
- Two codes, Barracuda VR and MFIX will be used in this study with more focus on Barracuda VR
- Description of heterogeneous chemical reactions and sulfur chemistry will be investigated and enhanced as the codes allow

	Year 1	Year 2	Year 3
Enhancement of coal devolatilization and char oxidation for chemical looping system analysis	■		
Implementation of metal oxide description and reaction		■	
Development and implementation of sulfur reduced mechanism	■		
Comparison of old and improved simulations of chemical looping PDU			■

Task 4 Approach

Improved Implementation of Reactions in Simulations

- Led by Reaction Engineering International
- Close collaboration with CPFD Software, Inc.
- Heterogeneous chemistry
  - Coal devolatilization:

    $$(\text{raw coal}) \rightarrow Y_{vol}\text{Volatiles} + (1-Y_{vol})\text{Char}$$

  - Char oxidation:

    $$C + [(1+\psi)/2]O_2 \rightarrow \psi CO_2 + (1-\psi)CO$$

  - Oxygen carrier's reduction and oxidation:

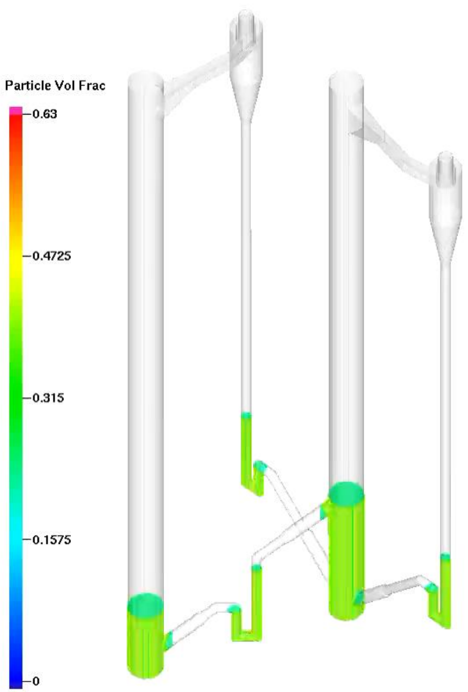
    $$Me_xO_y \leftrightarrow Me_xO_{y-1} + ½\, O_2$$

- Development and implementation of sulfur reduced mechanism to describe the heat release kinetics as well as the finite rate kinetics controlling gas phase sulfur species

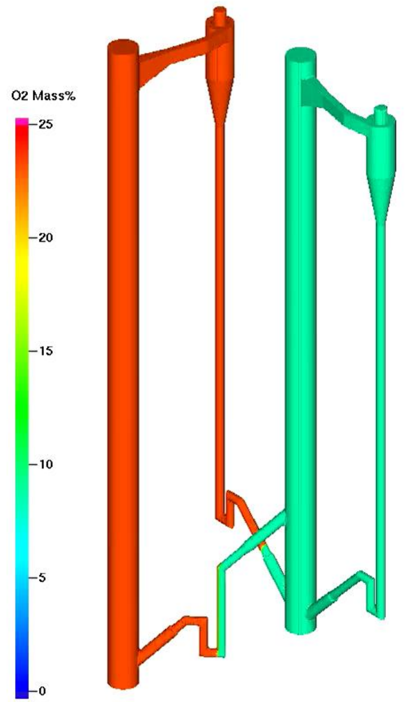
Reaction	Reaction Stoichiometry
Combustion of carbon monoxide	$2CO+O_2 => 2CO_2$
Forward water-gas shift	$CO+H_2O => CO_2 + H_2$
Reverse water-gas shift	$CO_2+H_2 => CO_2+H_2O$
Combustion of hydrogen	$H_2+0.5O_2 => H_2O$
Combustion of methane	$CH_4+2O_2 => CO_2+2H_2O$
Combustion of coal	$C+O_2 => CO_2$
Copper decomposition	$2CuO => 0.5O_2 + Cu_2O$
Copper oxidation	$Cu_2O + 0.5O_2 => 2CuO$

Task 4 Results

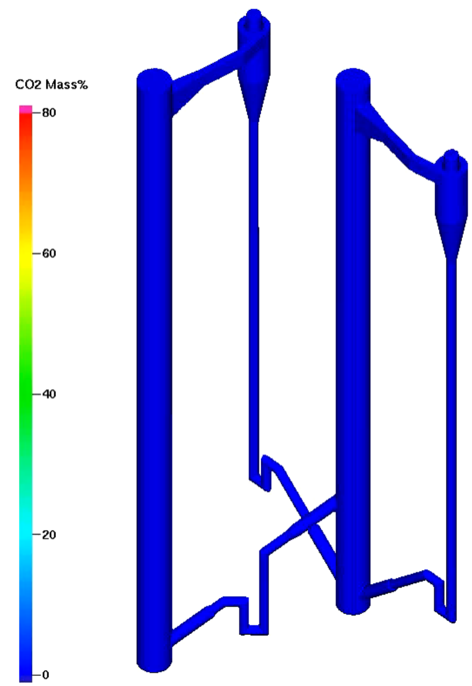
Improved Implementation of Reactions in Simulations



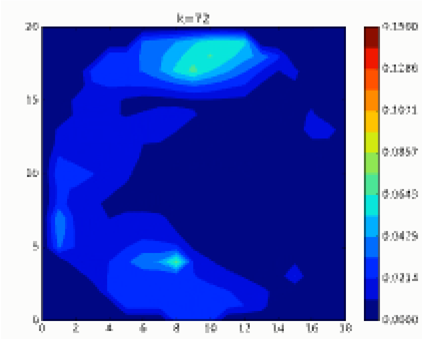
Particle volume fraction



Oxygen



Carbon Dioxide



Methane in Fuel Reactor

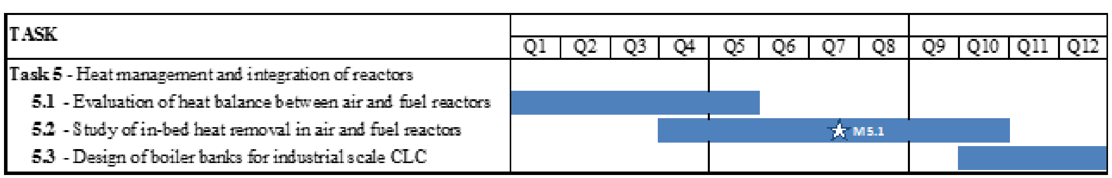
'k' = cell number (bottom to top)

Coal fed on right side

Task 5:
Heat Management and Integration of Reactors

5. Heat Management and Integration of Reactors
- 5.1 Evaluation of heat balance between air and fuel reactors
- 5.2 Study of in-bed heat removal in air and fuel reactors
- 5.3 Design of boiler banks for industrial-scale CLC

- Objective: Evaluate heat extraction from CLC system with an eye towards steam generation in next-scale and power generation in utility-scale systems
- Approach
  - Computational modeling of heat balance in the air reactor/fuel reactor system as well as steam and power generation in a CLC-based power plant
  - Practical implementation of heat extraction from CLC reactors



Task 5:
Heat Management and Integration of Reactors

- Process modeling
  - Develop heat and mass balances, updating as more information is gained on oxygen carrier performance and operating conditions
- Experimental evaluation
  - Design and install heat extraction units in air and/or fuel reactors of PDU system
  - Evaluate heat transfer, system performance, temperature control, local bed particle performance
  - Data for design of heat extraction systems for larger-scale systems
- Reactor simulation
  - Investigate effect of in-bed and freeboard tube bank configurations on hydrodynamics and particle flows

Status of Task 5:
Heat Management and Integration of Reactors

- Aspen model of two reactors
  - Includes heat exchangers for heat addition/removal
  - Consideration of where best to remove heat
    - Loop seals?
    - Within bed?
  - Identification of operation regimes vs reactor heat needs
    - Both reactors exothermic
    - One reactor requires heat input
    - Both reactors require heat input

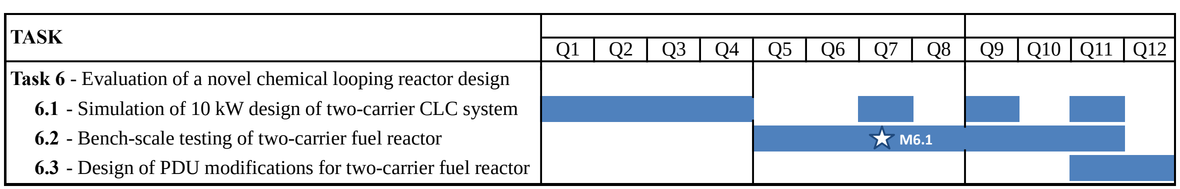
- Study of fluidized bed combustor heat removal schemes
  - In-bed and freeboard heat recovery
  - Downstream heat recovery

Task 6: Evaluation of Novel Chemical Looping Reactor Designs

6. Evaluation of Novel Chemical Looping Reactor Designs

- 6.1 Simulation of a 10 kW two-carrier system
- 6.2 Bench-scale testing of a two-carrier fuel reactor
- 6.3 Design of PDU modifications for two-carrier fuel reactor

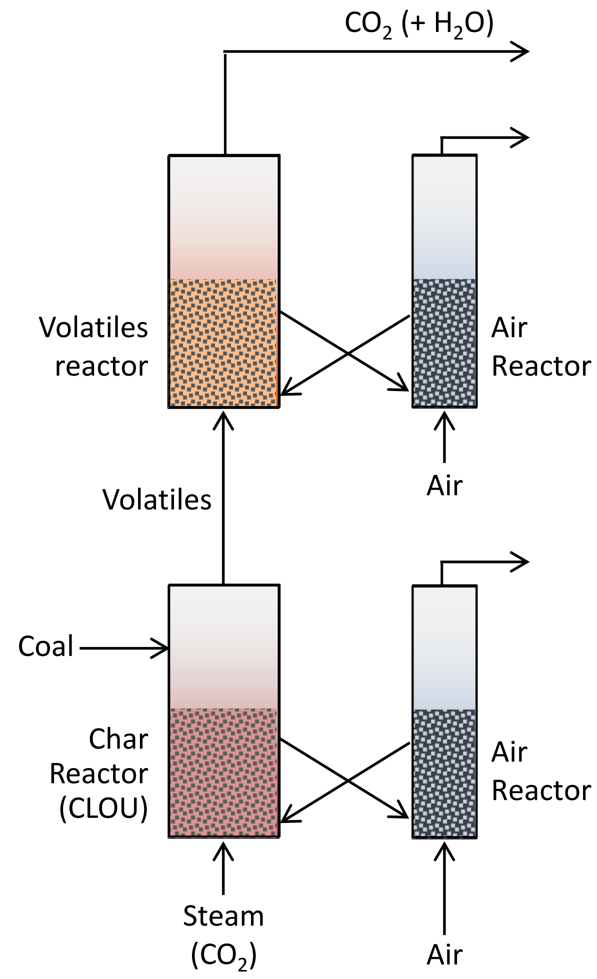
- Objective: Investigate performance of alternative reactor configurations for CLC and CLOU
- Approach
  - Reactor simulation and process modeling
  - Experimental evaluation in 10 kW CLC system



Task 6:
Evaluation of Novel Chemical Looping Reactor Designs

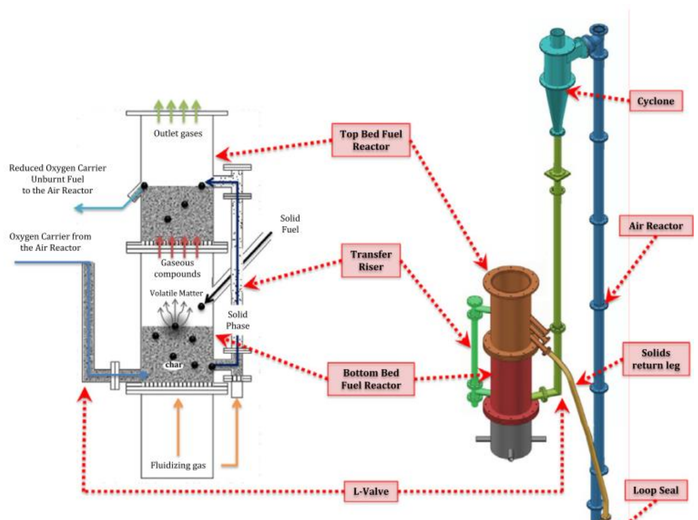
- Two-carrier fuel reactor
  - Char reactor
    - Coal fed onto top of char reactor
    - Take advantage of O_2 release of CLOU carrier to convert unreactive char in one reactor
      - Copper-based
      - Other CLOU carriers (Mn-Fe)
  - Volatiles reactor
    - Situated above/downstream of char reactor
    - Use conventional CLC carrier to convert volatiles
    - Less expensive carrier
  - Two carrier cycles and air reactors

- Approach
  - Reactor simulation and process modeling
  - Experimental evaluation in 10 kW CLC system

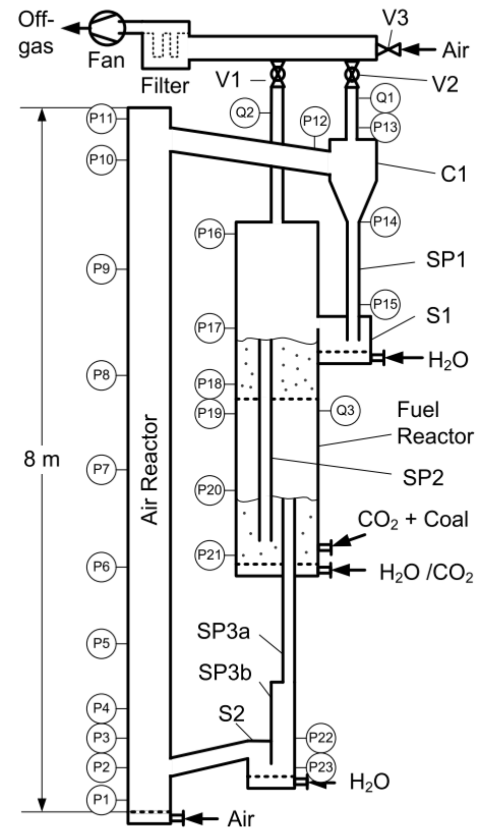


Status of Task 6:
Evaluation of Novel Chemical Looping Reactor Designs

- Literature review
- Simulation of existing 10 kW reactor
- Lab-scale char conversion analysis



From Coppola et al. (2015)



From Thon et al. (2014)

A. Coppola et al., *Applied Energy* 157(2015) 449-461.
A. Thon et al., *Applied Energy* 118(2014) 309-317.

Progress and Current Status:
Significant Accomplishments

- Evaluation of oxygen carrier/ash interactions
  - Good agreement between models and experiments
- Effective separation of Cu from spent oxygen carrier
- Improved operation of loop seals
- New solid separation system developed
- Improved implementation of chemical reactions in simulations

Future Plans

- **This project**
  - Design for copper recovery and recycle system
    - Bench-scale testing
  - Installation of disengager
    - Cold flow model
    - PDU
  - Evaluation of heat removal from PDU
    - Heat panels for local heat removal/design data
  - Test 2-fuel reactor design at bench scale
- **Future development**
  - Continued operation and experience with PDU
  - Acquisition of validation data

Acknowledgments

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- Boise State University
- CPFD Software, Inc.

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