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Integrated Oxygen Production and CO_2 Separation through Chemical Looping Combustion with Oxygen Uncoupling

Project DE-FE0025076

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**Now at Boise State University, Idaho*

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Outline

- Project overview
- Technology background
- Technical approach / project scope
- Progress and current status of project
- Future plans

Project Overview

Participants: The University of Utah; Amaron Energy

Funding:

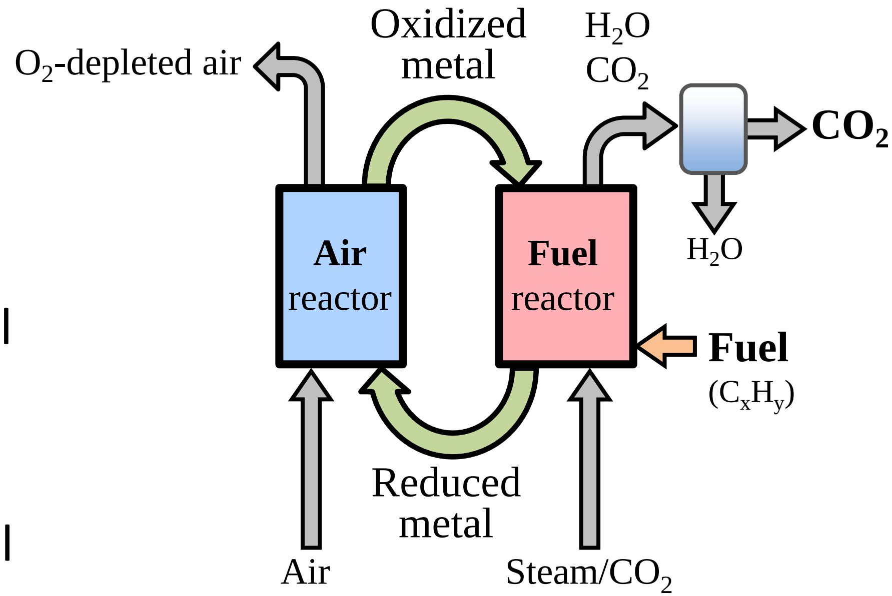
Source	University of Utah	Amaron Energy	TOTAL
DOE	$ 1,597,665	$ 282,655	$ 1,880,320
Cost share	$ 399,416	$ 70,664	$ 470,080
TOTAL	$ 1,997,081	$ 353,319	$ 2,350,400

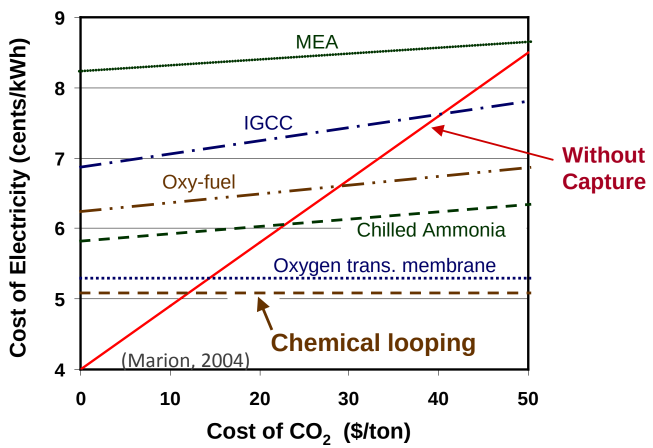
Project Dates: September 1, 2015 – September 30, 2018

Objectives: Advance chemical looping combustion with oxygen uncoupling (CLOU) technology to pilot scale (NETL TRL 5) through system scale-up, operation of a 200 kW process development unit, process modeling and reactor simulation

Technology Background: Chemical Looping Combustion (CLC)

- CLC achieves *in situ* air separation by using a metal to transport oxygen from *air reactor* to *fuel reactor*
- Fuel (e.g. natural gas, coal) fed to fuel reactor is indirectly combusted by oxygen on oxidized metal
- Metal returns to reduced state in fuel reactor and “loops” back to air reactor
- Overall balance same as for conventional combustion
- Economic evaluations indicate CLC yields lowest COE of any CO_2-capture technology

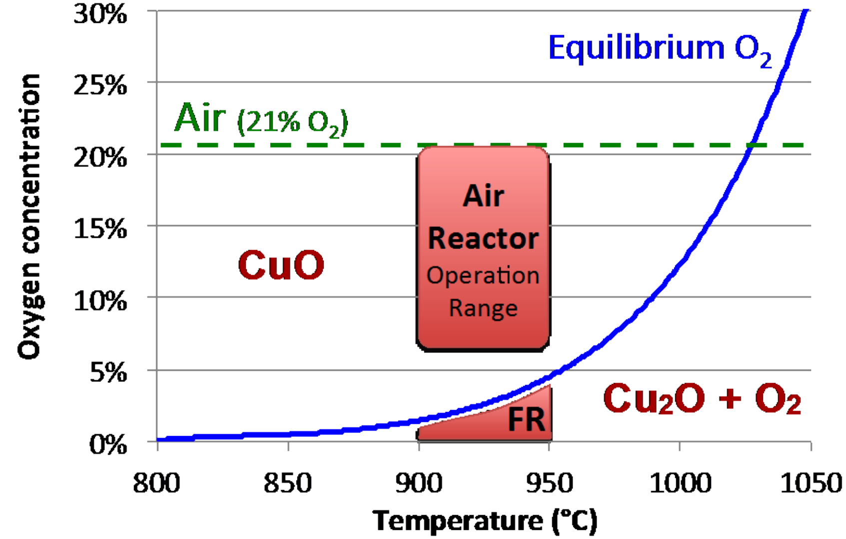


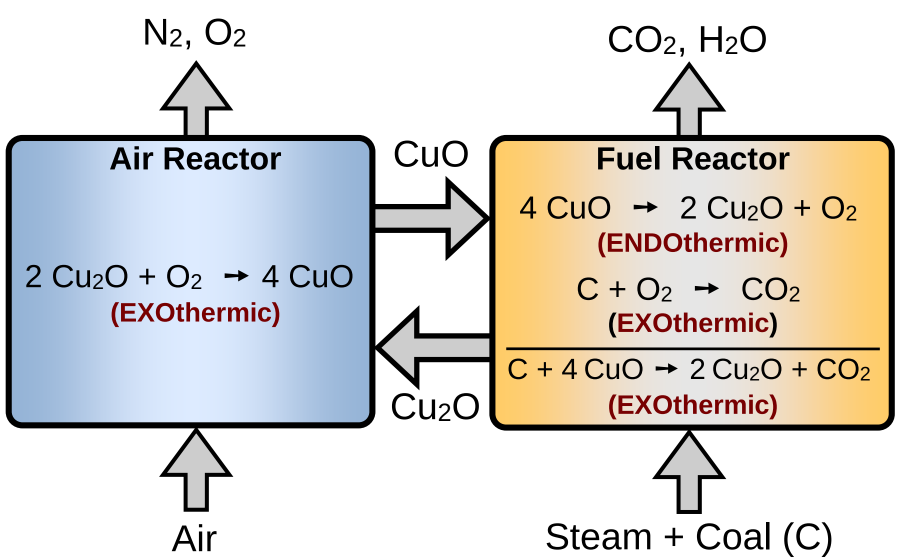


Technology Background: Fundamental Science Chemical Looping with Oxygen Uncoupling (CLOU)

$Cu_2O(s) + ½ O_2(g) \rightleftarrows 2 CuO(s)$

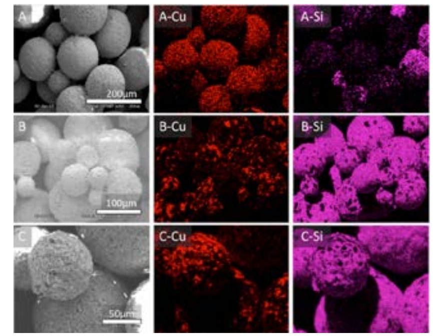
- Copper is one of few metals for which oxidation equilibrium (Cu_2O/CuO) lies within CLC operating temperatures.
- Cu_2O is oxidized in air reactor
- CuO spontaneously releases O_2 in fuel reactor due to low O_2 partial pressure
- Released O_2 reacts with solid coal char, converting more than 50x faster than with non-CLOU oxygen carriers

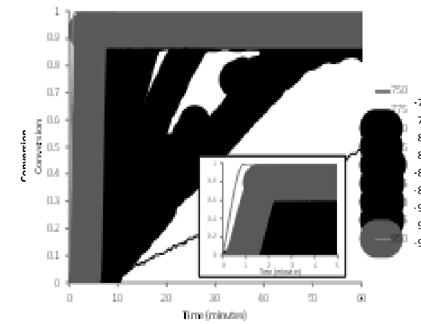


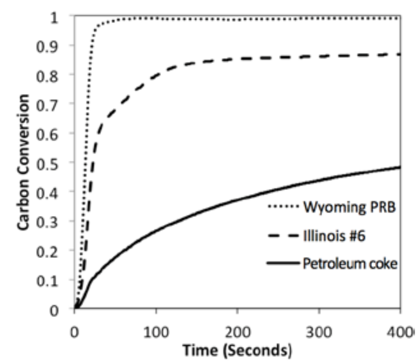


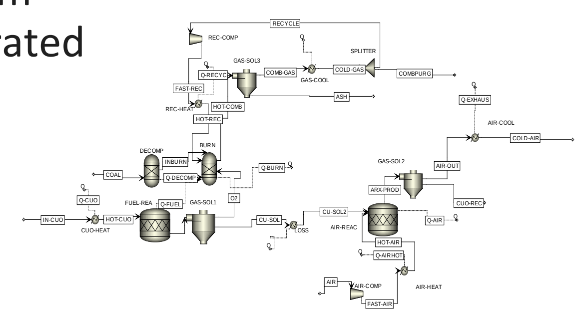
Technology Background: Previous R&D at University of Utah

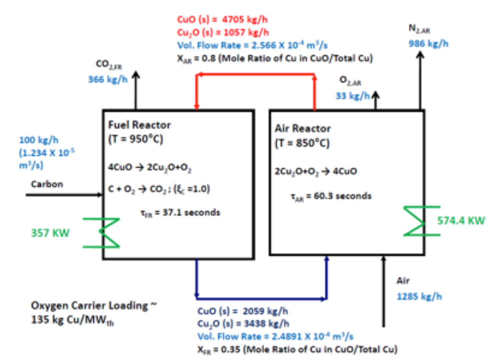
- **CLC intensively researched worldwide**
  - UofU researching since 2007
- **Oxygen carrier development**
  - Focus on <u>inexpensive</u> copper-based carriers with <u>scalable</u> production
  - Dozens of alternatives tested
  - Baseline is CuO-on-SiC/SiO_2
- **Reactor and process development**
  - Fundamental studies of CLOU reaction kinetics
  - Lab-scale experiments of coal conversion
  - Design and preparation of 200 kW PDU
- **Process modeling and reactor simulation**
  - Aspen Plus modeling of CLC system
  - Barracuda VR® modeling of integrated fluidized bed system











Technology Background:
Advantages and Challenges of CLOU

- **Advantages**
  - CLOU can convert coal char up to 50 times faster than conventional CLC
    - Carbon conversion > 99.9% has been achieved in bench-scale tests
    - CO_2 capture > 99% has been achieved in bench-scale tests
    - High conversion in fuel reactor eliminates need for carbon stripper
  - Fast reactions reduce reactor size and oxygen carrier inventory
  - High conversion and CO_2 capture improves economics

- **Challenges**
  - Operation of dual fluidized bed
    - Circulation, temperature control, particle retention
  - Oxygen carrier production
    - Balance copper availability, reactivity, physical strength
  - CLOU carriers are comparatively expensive
    - Physical robustness and retaining activity are especially important

Technical Approach

- **Three major research areas**
  1. Scale up of CLOU oxygen carrier production
  2. CLOU Experiments
     - 200 kW PDU
     - 10 kW bench-scale
  3. System modeling and reactor simulation

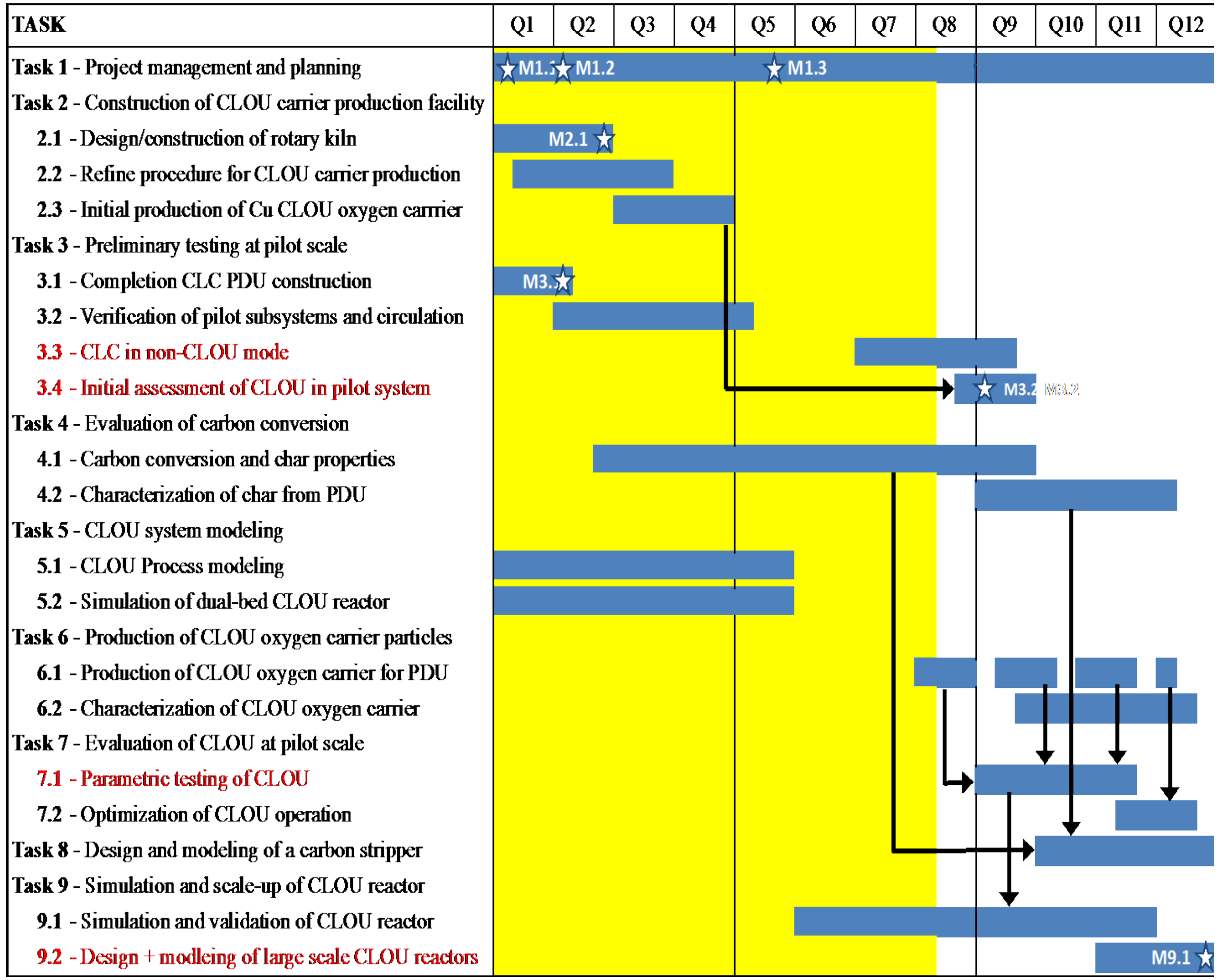
- **Performance targets**
  - CO_2 capture (target min. 90%)
  - CO_2 purity (target min. 95%)
  - Coal conversion (target min. 99%)

Work plan / Tasks

1. Project management
2. Construction of pilot-scale rotary kiln for oxygen carrier production ✓
3. Complete construction/initial testing of pilot-scale CLC system ✓
4. Evaluation of carbon conversion in CLOU environment
5. CLOU system modeling ✓
6. Production and characterization of CLOU carrier particles
7. Evaluation of CLOU performance and CO_2 capture at pilot scale
8. Carbon stripper design and modeling
9. Design of pilot/demo scale CLOU reactors

Project Scope:
Schedule, Milestones, Success Criteria, Risks

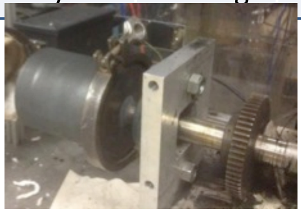
- **Technical milestones**
  - 2.1 Complete pilot rotary kiln
  - 3.1 Complete CLC PDU
  - 3.2 Start CLOU testing
  - 8.1 Carbon stripper installed
  - 9.1 Large CLC system design
- **Success criteria** focus on PDU
  - Key operation steps (tasks in red) require that specific performance can be achieved
- **Technical risks**
  - CLOU carrier unsuitable
    - Target lower Cu loading
  - Inadequate pilot performance
    - Component redesign
  - Excessive carrier attrition/loss
    - Reduce velocity, produce more carrier, find alternates



Progress and Current Status:
Scale-up of CLOU Oxygen Carrier Production

- **Equipment**
  - 0.1 kg lab scale rotovap
  - 1 kg lab scale
  - 10 kg bench scale
  - 100 kg pilot built (Amaron)
- **Manufacture**
  - Wet or dry impregnation
  - Support material is key
    - strong
    - inert
    - reasonable surface area
  - Complexes and stabilizers
  - Calcining
    - nitrate decomposition

System	Type	Capacity	Heating	Max T	Length	Diam
RV-1	Rotary evap	1 kg	Water bath	95°C	n/a	0.15 m
RK-1	Rotary kiln	1 kg	Elec Inductive	800°C	0.15 m	0.1 m
RK-10	Rotary kiln	10 kg	Elec radiative	350°C	0.8 m	0.2 m
RK-100	Rotary kiln	100 kg	Natural gas	500°C	1.4 m	0.4 m

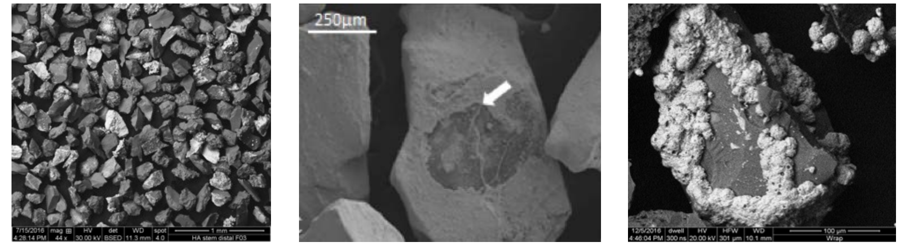

RK-1 lab-scale induction kiln

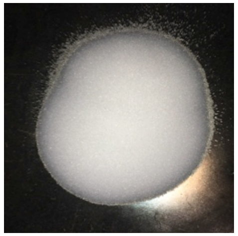

RK-10 bench-scale rotary kiln

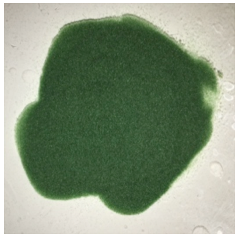

RK-100 oxygen carrier production kiln

Progress and Current Status:
Improvement of CLOU Oxygen Carriers

- **Status**
  - Over 55 carriers tested
  - Baseline support: SiC
    - cheap but poor Cu distribution
  - New supports: SiO_2, $MgAl_2O_4$
    - also with stabilizers
  - Test batches of 50 kg produced
  - Good cyclability in small fluid bed
- **Characterization**
  - TGA: oxygen loading/rates
  - BET: surface area
  - SEM: morphology, Cu distribution
  - Crush strength
  - Lab-scale fluidized bed for long-term performance in a cycling fluidized bed reactor




Silica support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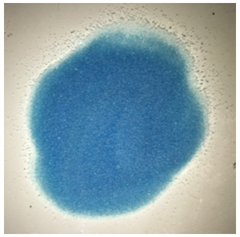
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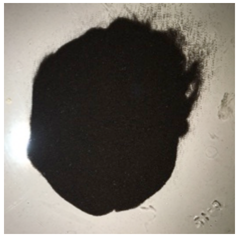
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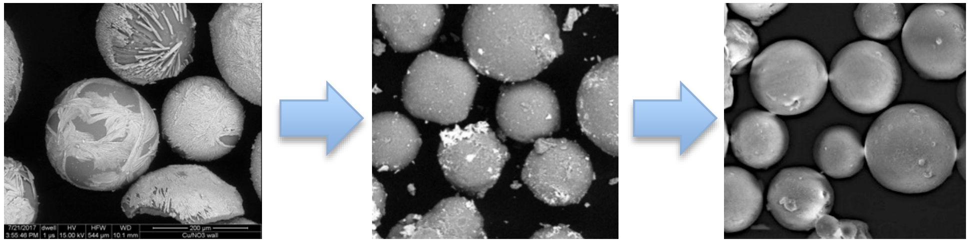
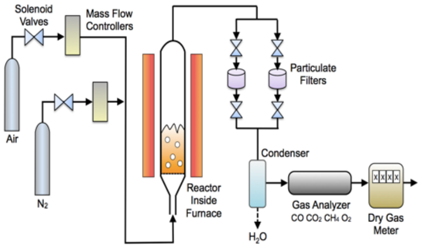
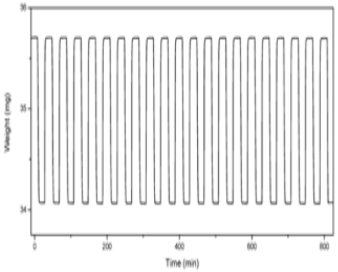


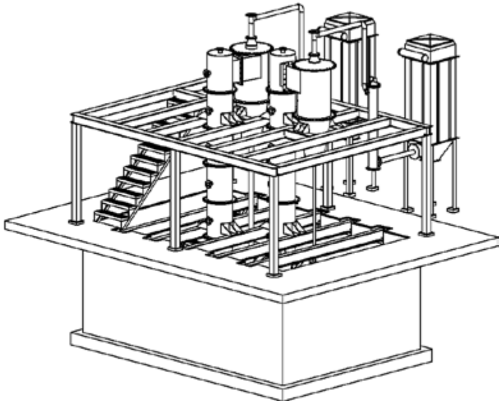

Lab-scale fluidized bed system

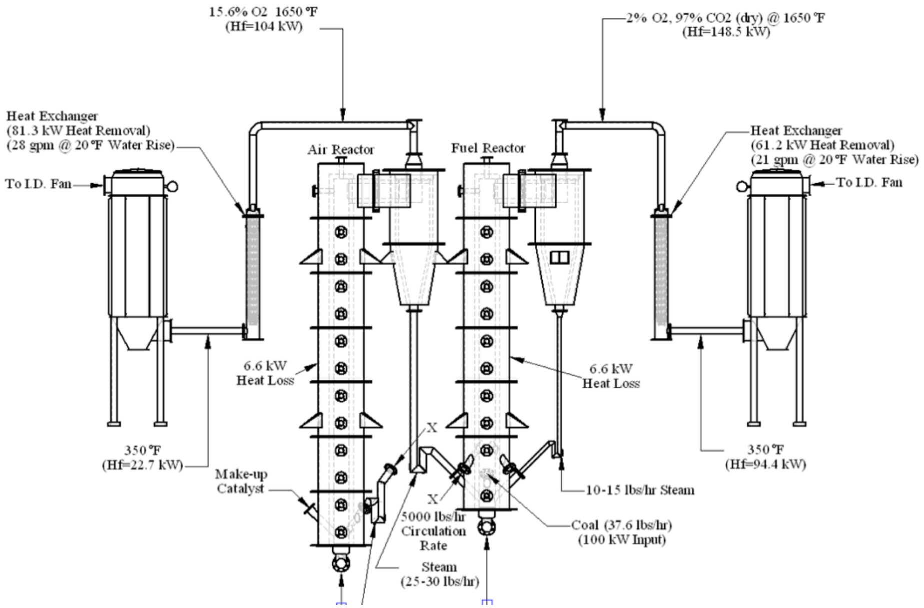




Progress and Current Status:
CLOU Experiments and Process Development

- **10 kW Bench Scale**
  - Approx 1.5 kg/hr
  - Two bubbling beds
  - All electrically heated
  - Screening studies
- **200 kW PDU**
  - Two interconnected CFBs
  - 0.25m ID, 5m tall
  - Air for AR, steam for FR
  - Refractory-lined
  - Electric + gas air/steam preheat
  - Approx. 175 kg bed inventory
  - Baghouse filters



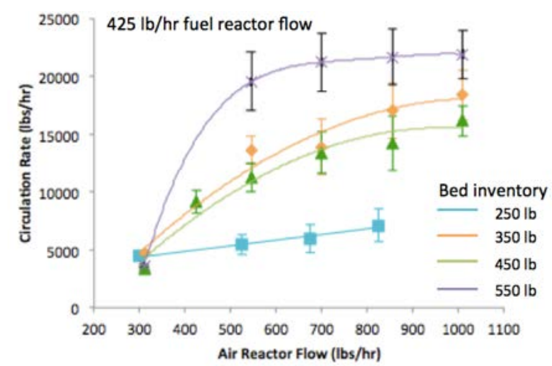


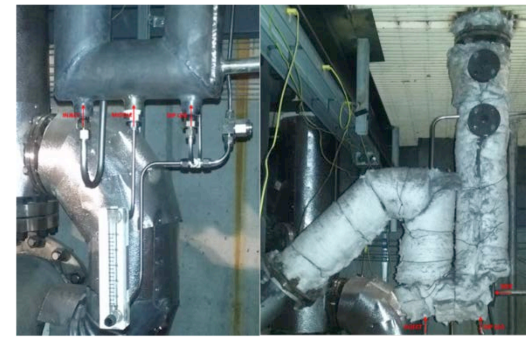
Progress and Current Status:
PDU Operation

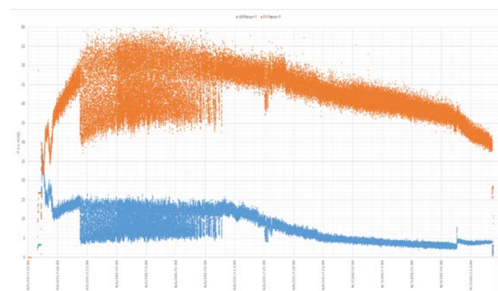
- Preliminary testing
  - Cold flow circulation rates
  - Hot flow circulation rates
  - Ilmenite as oxygen carrier
- Operation progression
  - CLC of natural gas
    - ilmenite
    - Cu-on-Al_2O_3
  - iG-CLC of coal
    - ilmenite
    - Cu-on-Al_2O_3
  - CLOU of coal
    - CLOU carrier

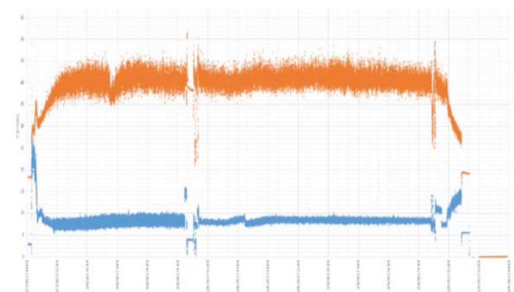
Progress and Current Status:
PDU Operational Experience

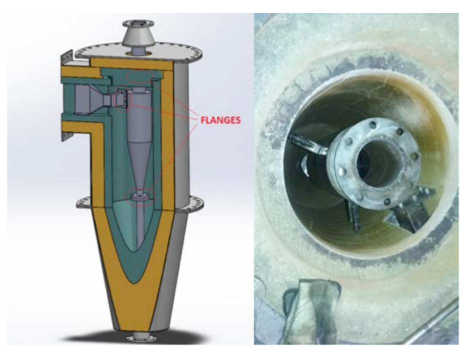
- **Status**
  - Construction complete
  - Shakedown complete
    - Gas flow + preheat
    - Controllable coal feed
    - Circulation rates > 10 ton/hr
  - Over 600 hours of hot circulation
  - Temps to 1700°F achieve
  - Operators comfortable
- **Challenges**
  - Preheat
    - electric, burners, propane, nat gas
  - Cyclones and bed loss
    - Geometry vs wall roughness
    - Loop seal operation
    - Loop seal sensors
    - Particle size
  - “Normal” things
    - Leaks, etc.





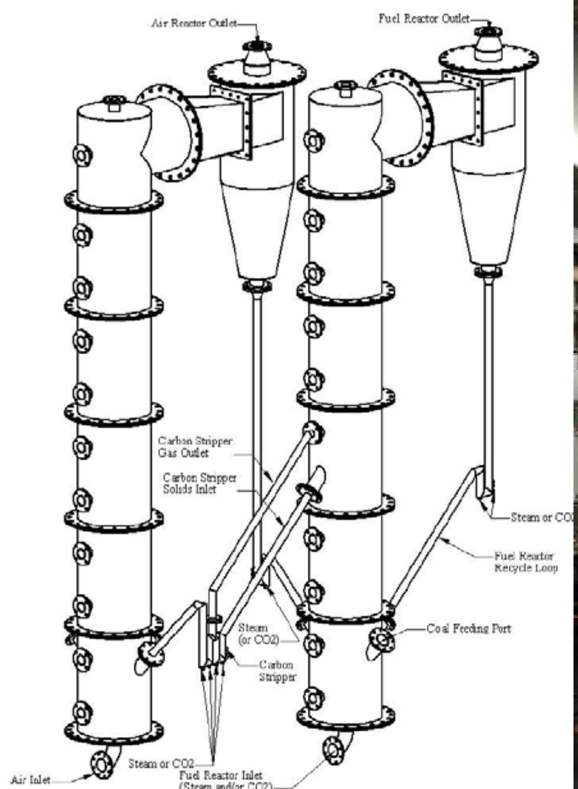


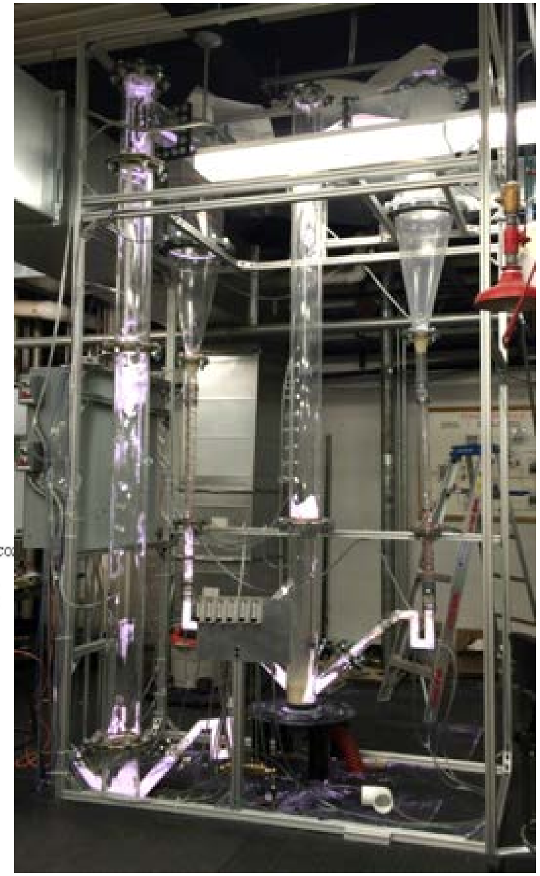




Progress and Current Status:
Process Modeling and Simulation

- **Experimental modeling**
  - Plexiglas cold flow system
  - Scaled properly to represent PDU
  - 60% scale
  - Air for fluidization
  - Glass beads
  - Pressure profiles
  - Circulation rates
- **Computational simulation**
  - CPFD Barracuda VR®

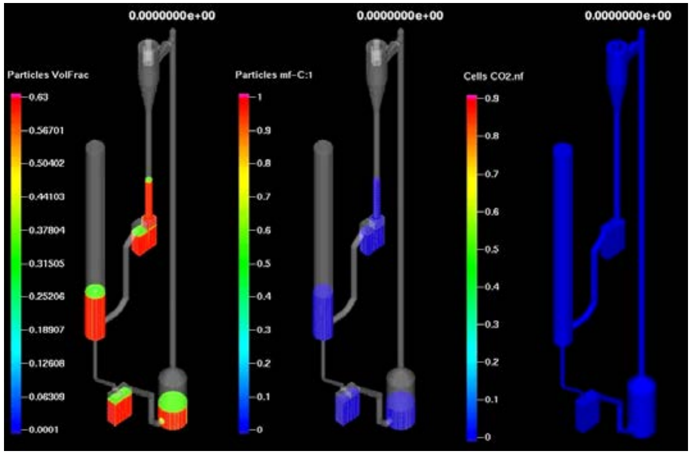


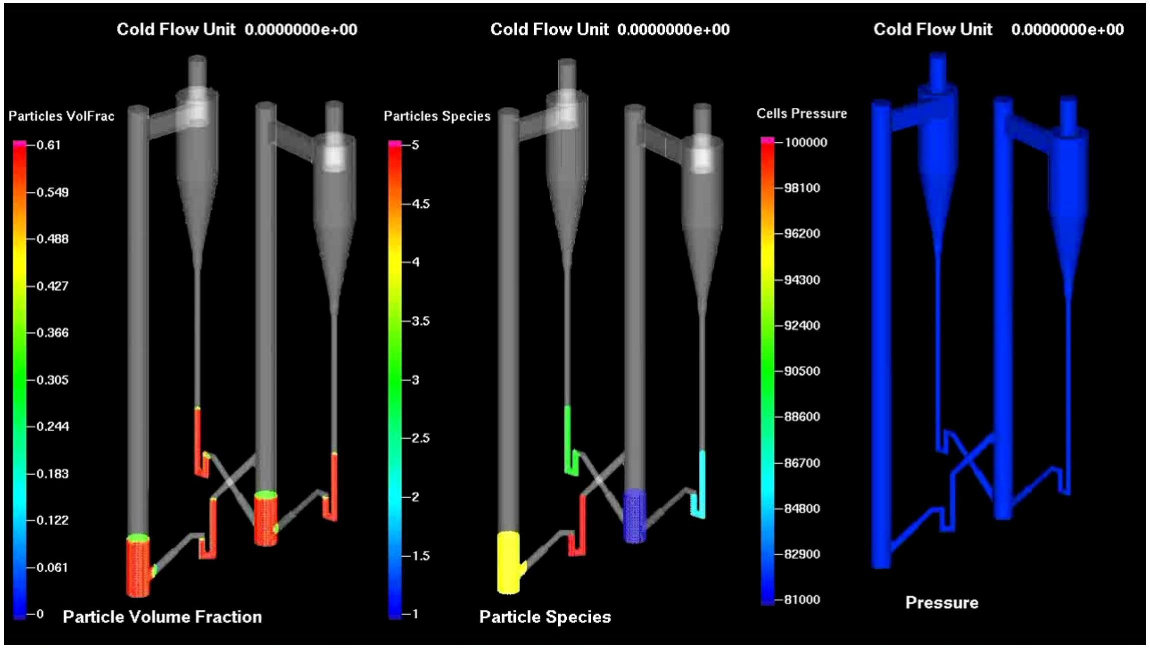


Cold-flow model of UofU PDU

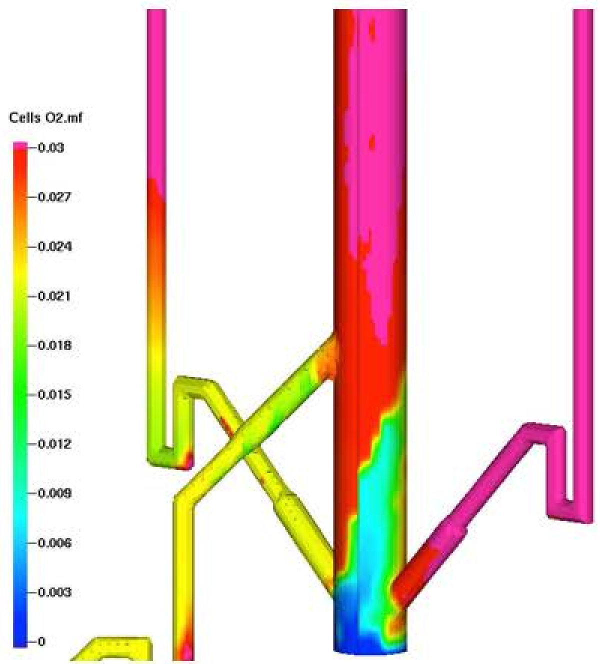
Progress and Current Status:
Chemical Looping Reactor Simulation

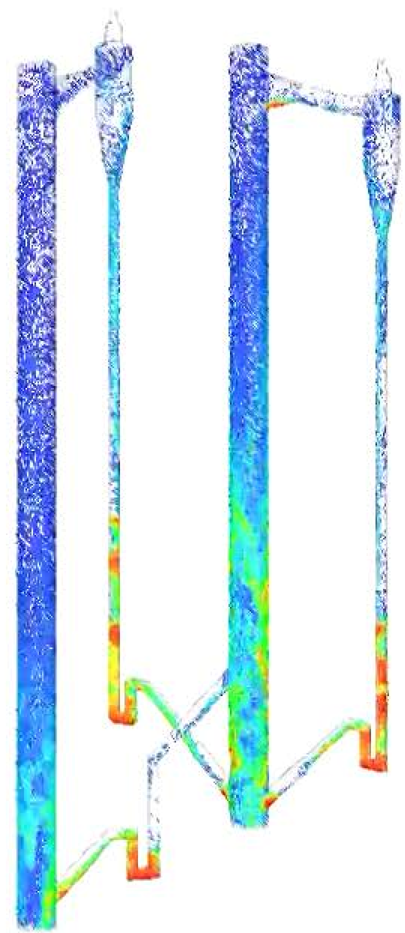
- Models of 10 kW bench-scale, 200 kW pilot-scale reactors, and cold-flow unit
- Simulations include
  - hydrodynamics
  - heat transfer
  - Chemistry/kinetics
    - Oxygen carrier
    - Coal combustion
    - Gas phase
- Understanding from simulations valuable for interpreting behavior of pilot-scale system



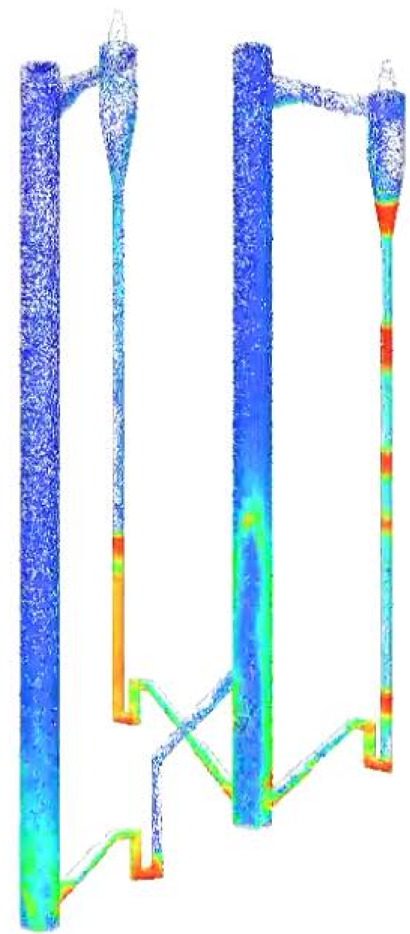


Progress and Current Status:
Simulation as an Aid for Development





Old carrier



New carrier

Progress and Current Status: Significant Accomplishments

- **Successful scale-up of CLOU oxygen carrier production**
  - Can now produce enough material for PDU operation
  - Initial batches of well-performing carrier to 20% CuO loading produced
- **Successful commissioning of 200 kW PDU**
  - All systems now function properly
  - Measured oxygen carrier circulation rates exceed design
  - Already 600+ hours of hot operation with circulation
  - Initial CLC experience with natural gas
- **Successful development of PDU simulation model**
  - Incorporation of kinetics for oxygen carrier reactions
  - Incorporation and improvement of coal combustion reaction kinetics
  - Over 50 different conditions have been simulated, each with at least 60 seconds of operation

Future Plans

- **This project**
  - Continue improving CLOU carrier performance
    - Improve physical and chemical stability
    - Eventually target 50+ % CuO to increase load
  - Parametric testing of PDU with CuO (CLOU) carrier and coal
    - Vary coal, coal particle size, air reactor flow rate (circulation rate),
    - Measure CO_2 capture, CO_2 purity, fuel conversion, overall performance
    - Design, install and test carbon stripper to improve coal conversion and CO_2 capture.
  - Advance computational simulation
    - Validate simulation of PDU with operational data
    - Simulate larger (e.g. 10 and 100 MW) reactors
- **Future development**
  - Continued operation and experience with PDU
  - Pursue opportunities for larger pilot (3-10 MW) system

Acknowledgments

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- University of Utah Chemical Looping team
- Amaron Energy

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