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

DE-FE0029160

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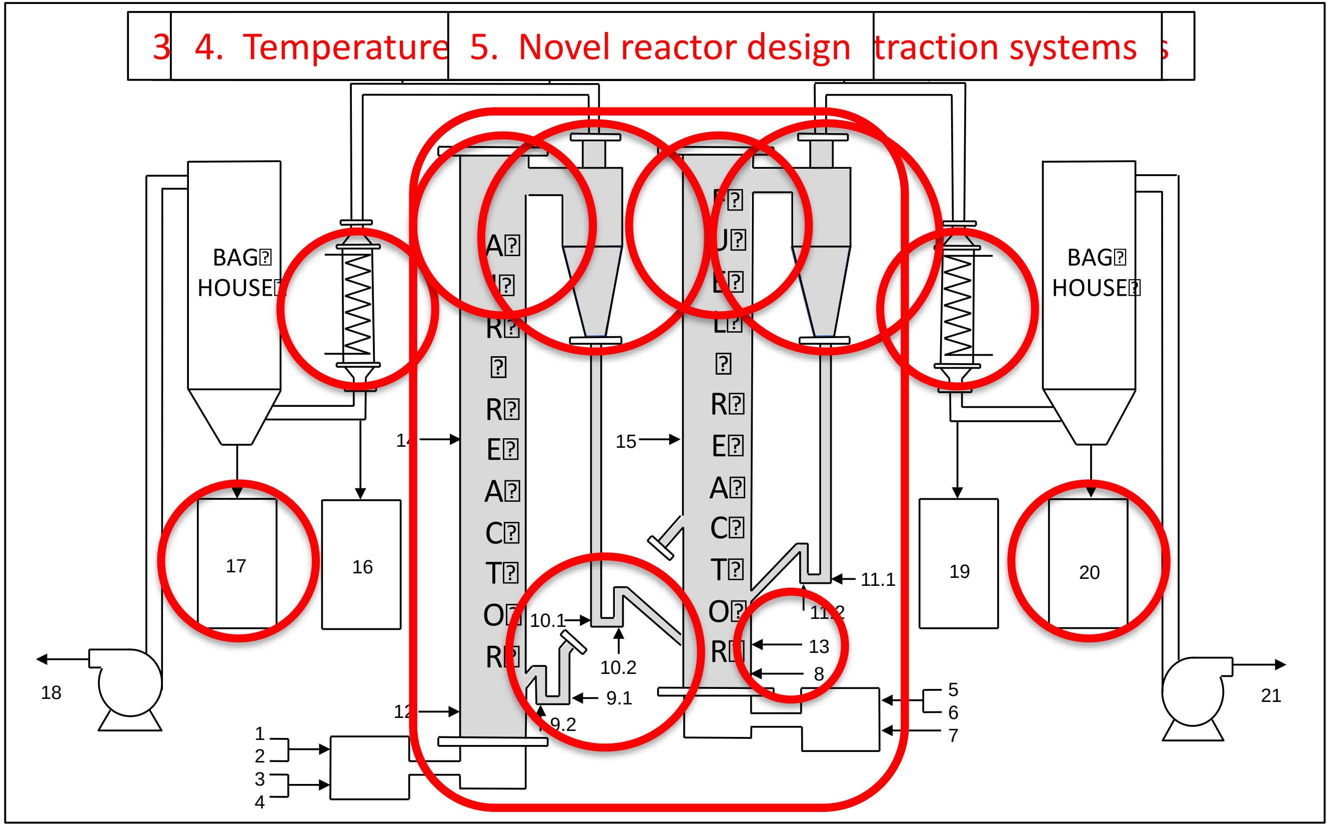
NETL Transformative Power Generation Project Review Meeting
28 September 2020

Project Summary

- Overall goal: Advance chemical looping combustion (CLC) and CLOU technology towards higher TRL
  - Meet DOE targets of at least
    - 90% CO_2 capture
    - 95% CO_2 purity
  - Reduce operating costs
  - Improve performance and reliability

- Scope:
  - 5 sub-projects (tasks)
  - Focus on industrially-relevant issues
  - Combine modeling, lab-scale studies, pilot tests
  - Use U Utah CLC PDU as test bed

Scope of Project / Focus Areas



Alignment with NETL/DOE Goals

ACS Program and FOA Objectives:

- Develop enabling technologies that address challenges with advanced combustion
- Improve the overall economics ensuring that performance and cost potential are substantially better than today's baseline pulverized coal power plant with post-combustion capture
- Support advanced combustion technologies by addressing critical technology gaps and improving overall system performance

Suggested research topics from FOA:

- Oxygen Carrier Improvement
- Gas/Solid Management
- Solids Separation
- Reactor Design
- Heat Management and Integration
- Sulfur Management
- Oxygen Carrier Regeneration
- Oxygen Carrier Manufacturing

Current Status of Project

- Progress
  - Lab-scale and modeling work mostly complete
  - Verification in PDU ongoing
  - Disruption this year due to COVID-related lab shutdowns
- On-track to meet performance benchmarks for CO_2 capture
- Changes in goals/objectives
  - Minor changes in research approach for some tasks
- Project update and new results on following slides

Development of Zero-Loss Oxygen Carrier Processing

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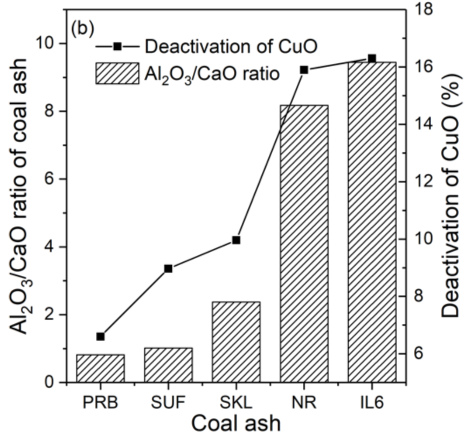
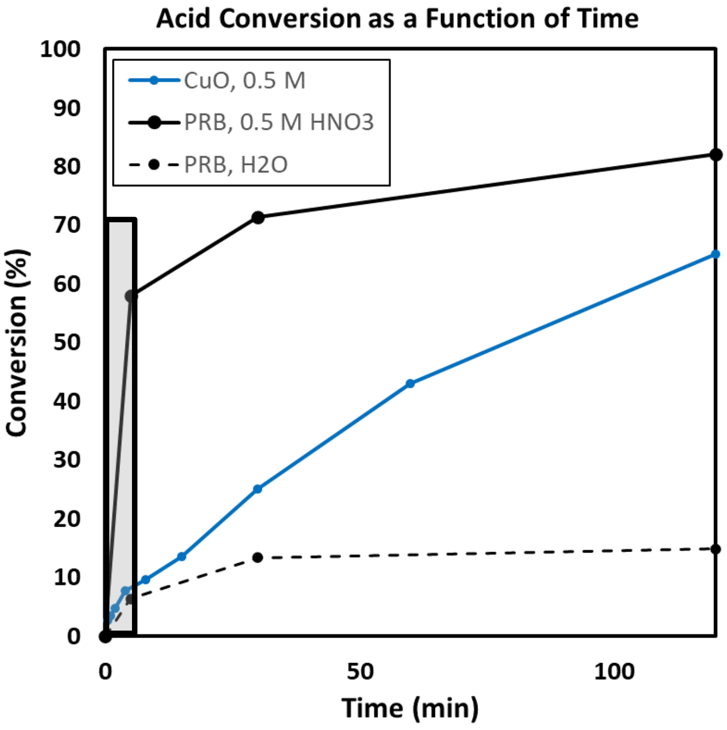
- Objective: Minimize make-up oxygen carrier requirements
- Three causes
  1. Loss of activity by reactions with coal ash creating new compounds
  2. Loss of activity due to agglomeration
  3. Loss of material through attrition and/or carryover
- Approach
  1. Modeling of solid-phase chemistry in reactor
     - Understand risk regimes
     - Propose methods to alleviate Cu deactivation
  2. Development of process to recover and recycle active metal (Cu)



OC Recycle – Leaching Studies

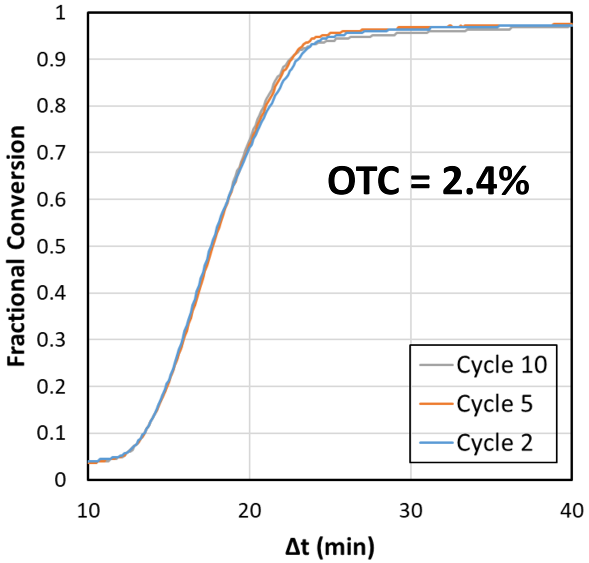
- 60 percent of PRB Black Thunder ash is leachable in nitric acid
  - 10% of the acid leachable fraction can be removed by water
- Dissolution of Illinois #6, Utah Skyline coal ashes is somewhat less
  - Conversion plots still resemble those of PRB ash (figure)
- Significant difference in conversion at 5 min
  - Approx 60% of PRB ash
  - Less than 10% of CuO removed
  - Ash more reactive → can remove ash into the aqueous phase with little CuO loss



OC Recycle – Leaching Studies

- Selective leaching of CuO from ash is viable – though 100% separation is not
  - Some impurities will be present in the $Cu(NO_3)_2$ leachate
- Many impurities improve carrier performance
- Less deactivation than pure CuO carrier
- Very consistent reduction reactivity
- Relatively high reduction rate

Reduction conversion for a 30% CuO carrier containing

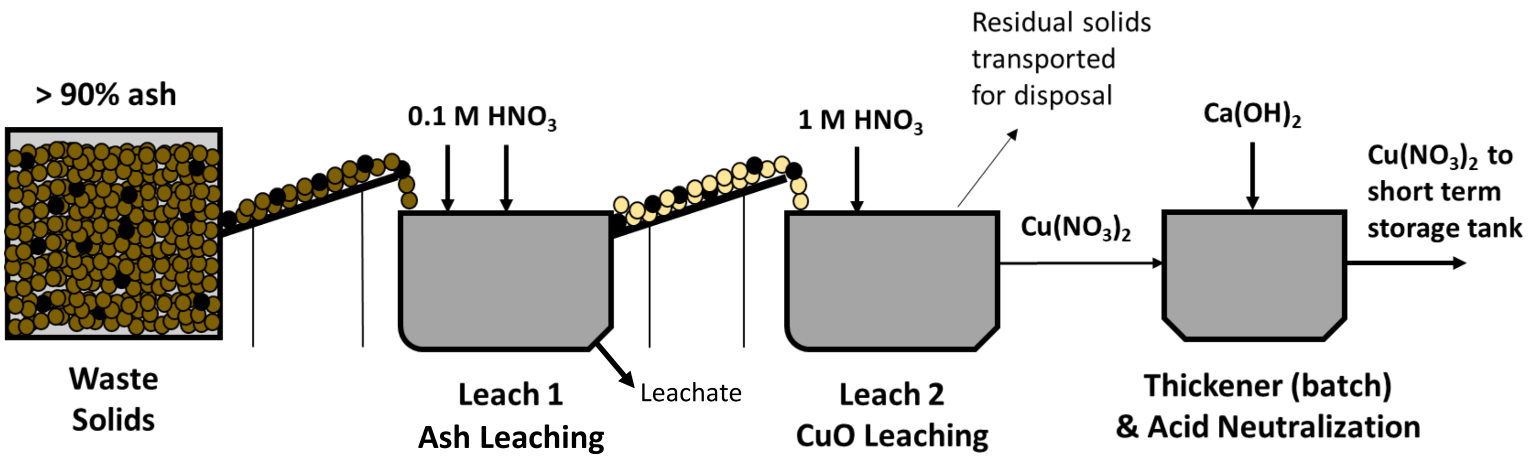


***Impurities include low concentration CaO, Fe_2O_3, Na_2O, etc.**

OC performance does not worsen after adding impurities → **low cost recycle viable**

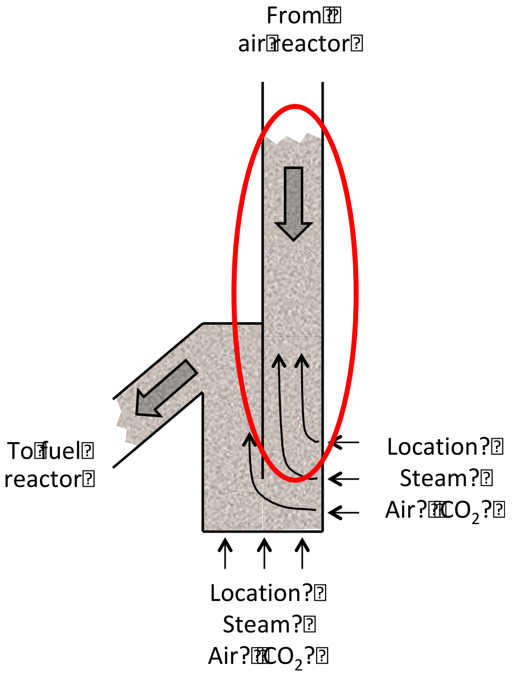
Conceptual Design of Pilot-Scale System

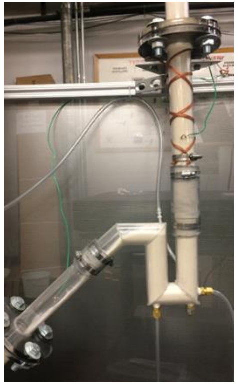
- Continuous vat leaching (CVL) best option
  - Consistent outlet properties
  - Flexible – easily accommodates different batches of waste solids
- 50 kg/day of semi-continuous operation
- Design also suitable for industrial scale
- Data from leaching studies will aid in deciding flow rates and vessel size
- Final $Cu(NO_3)_2$ stream will contain some impurities (subtask 2.2)
- Moderate $Ca(OH)_2$ addition will improve OC performance

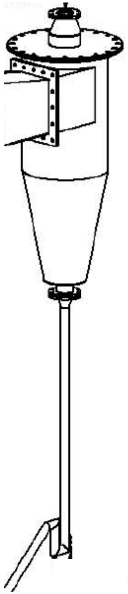


Technical Area 2:
Solids Transfer and Separation

- Objective: Improve performance through better control of particle circulation and gas-solid separation
- Loop seal design
  - Evaluate alternate designs
  - Consider gas environment
- Alternative gas-solid separation
  - Other cyclones
  - Disengagers
  - Ash/carrier particle separation

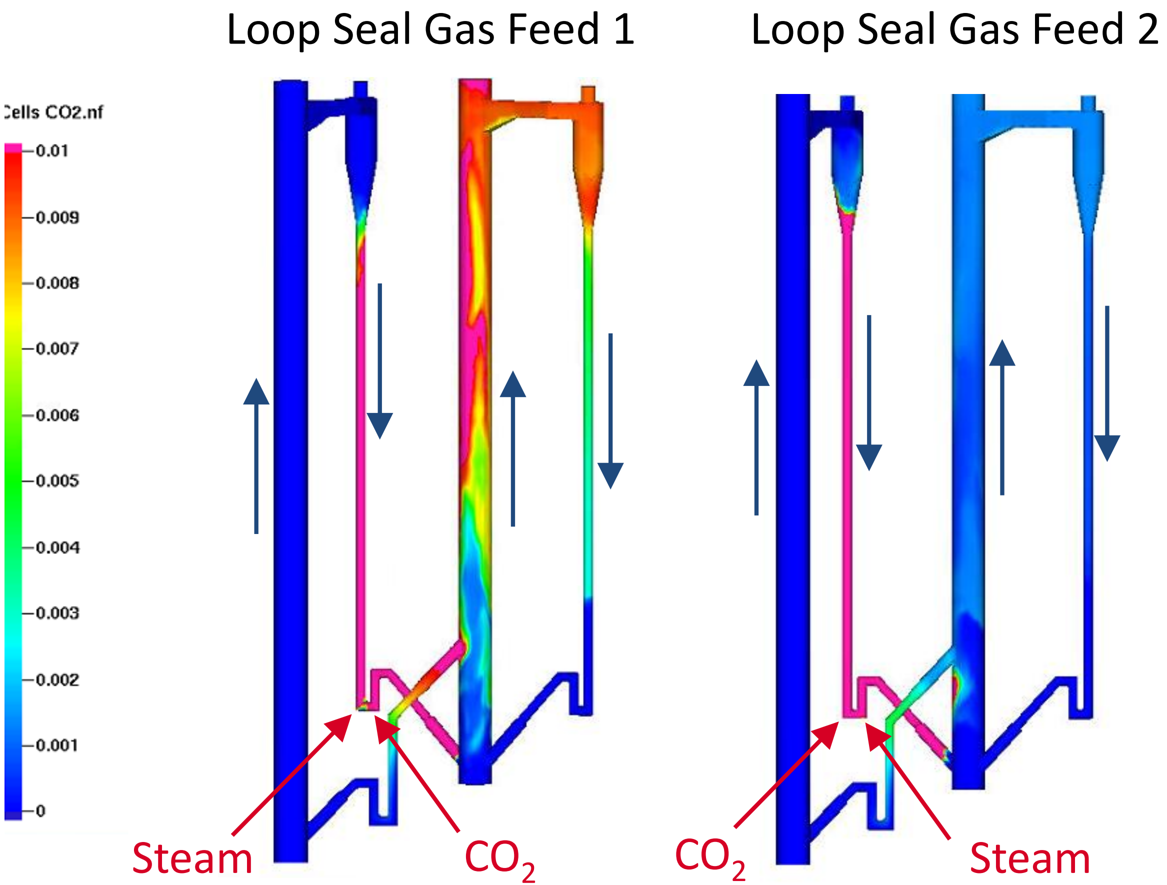






Concept → CFD Modeling → Cold-Flow → PDU

Tracking Loop Seal Fluidizing Gas

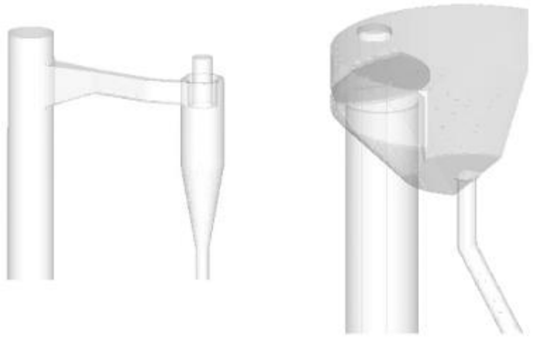


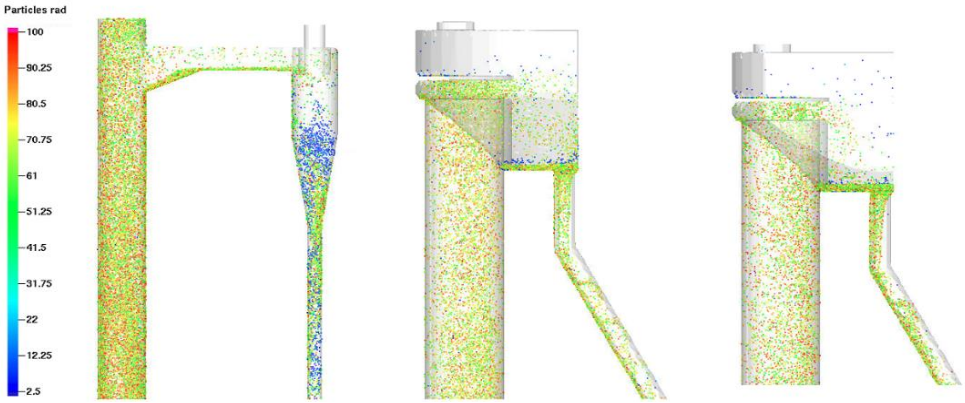
- Need to keep OC oxidized until entering FR
- Track flow of air (CO_2) introduced through loop seal
- Config 2 keeps OC oxidized while limiting O_2 in FR

Effectiveness of Ash/Oxygen Carrier Separation

Ash = 5-20 μm, OC = 100-200 μm

Cyclone | Disengager Design 1 | Disengager Design 2

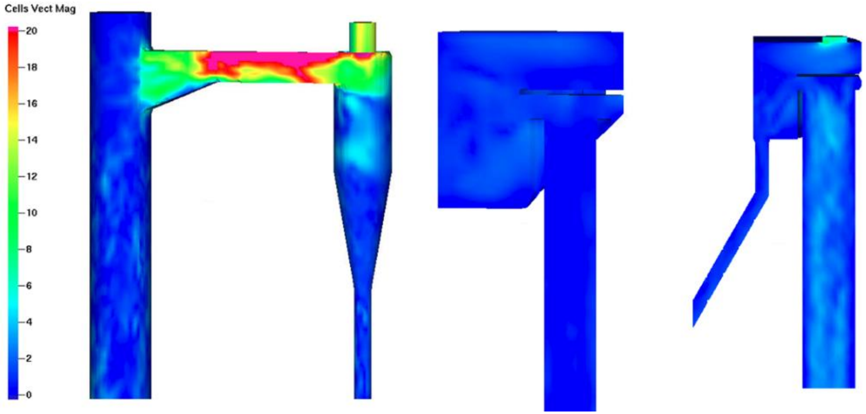




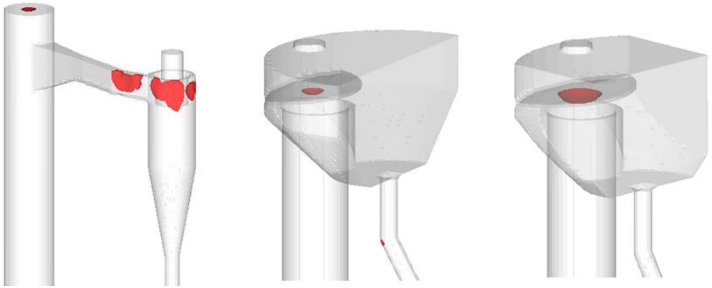
Separator	OC Recycle Efficiency	Ash Removal Efficiency
Cyclone	99.99%+	44%
Disengager – Large	99.99%+	68%
Disengager - Small	99.99%+	71%

The amount of OC circulating through the FR is much higher than the amount of ash, which allows for the disengagers to still maintain a high efficiency

Is Erosion a Concern?



Cross section of velocity magnitude (m/s)



High erosion areas are shown in red

- Erosion is proportional to impact angle and impact velocity.
- Because of the low speed due to the area expansion in the disengager, erosion is not significantly worse than in the cyclone

Technical Area 3:

Improved Chemistry and Reactions in Simulations

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- Led by Reaction Engineering International
- 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 reduction and oxidation:

    $$Me_xO_y \leftrightarrow Me_xO_{y-1} + \tfrac{1}{2} O_2$$

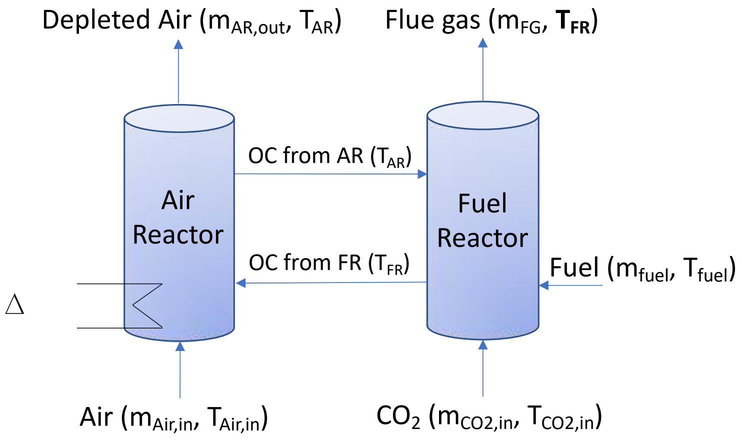
- Development and implementation of sulfur reduced mechanism
- Task completed

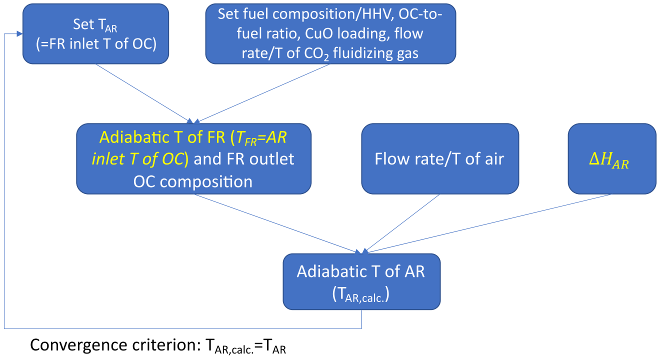
Reaction	Reaction Stoichiometry
Combustion of carbon monoxide	$2CO+O_2 \Rightarrow 2CO_2$
Forward water-gas shift	$CO+H_2O \Rightarrow CO_2 + H_2$
Reverse water-gas shift	$CO_2+H_2 \Rightarrow CO_2+H_2O$
Combustion of hydrogen	$H_2+0.5O_2 \Rightarrow H_2O$
Combustion of methane	$CH_4+2O_2 \Rightarrow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

Technical Area 4:

Heat Management and Integration of Reactors

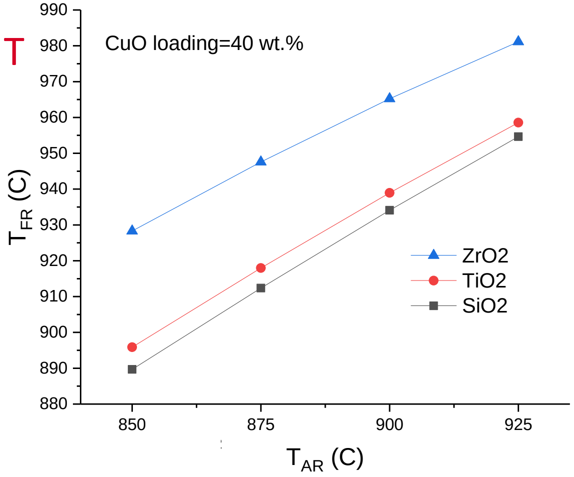
- Objective: Evaluate heat extraction from CLC system considering steam generation for power generation in large-scale systems
- Approach
  1. Computational modeling of heat balance in the air reactor/fuel reactor system as well as steam and power generation in a CLC-based power plant
  2. Experimental evaluation and measurement of heat transfer to tube banks/heat panels in PDU
  3. Simulation of heat transfer with experimental data for validation



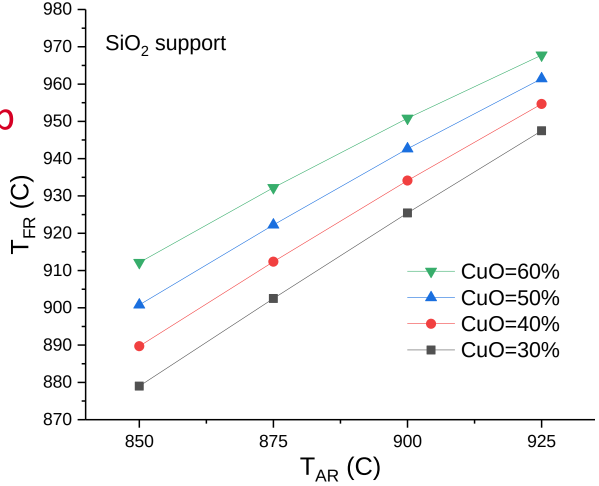


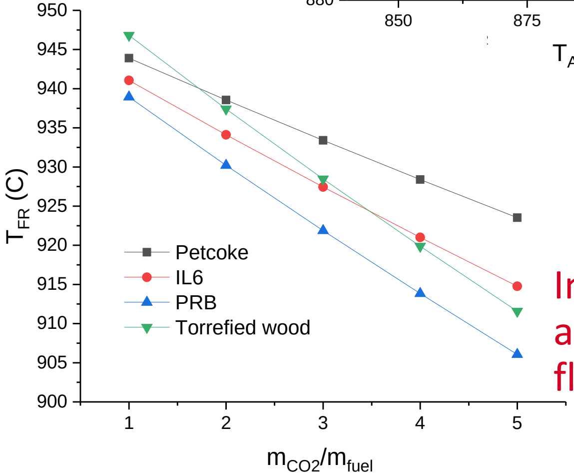
Modeling of Reactor Heat Balance

Influence of AR T and OC support on FR temp

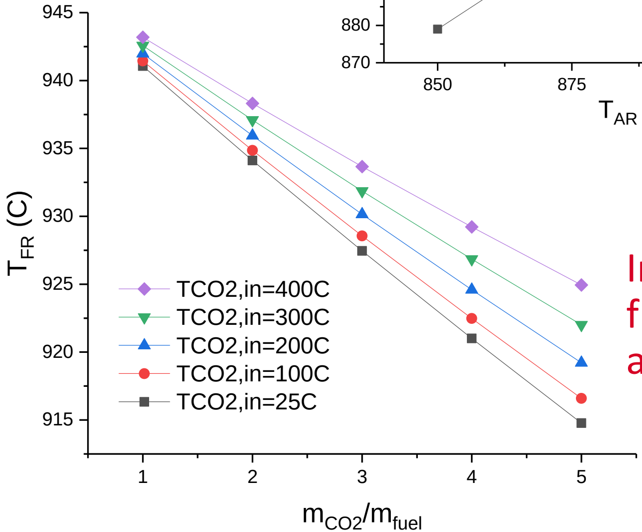


Influence of AR temp and OC CuO loading on FR temp





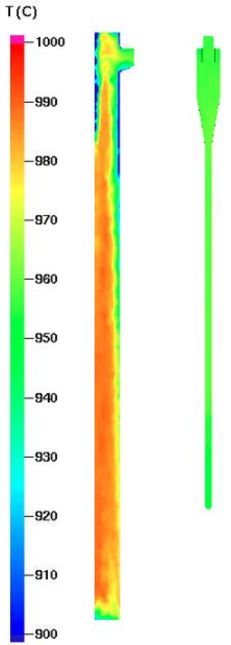
Influence of fuel and FR fluidizing gas flow on FR temp



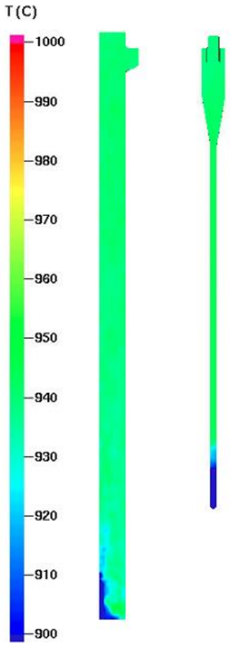
Influence of FR fluidizing gas flow and T on FR temp

Simulation of Heat Removal in AR

- Heat extraction somewhere in reactor necessary for temperature control
- Freeboard (top) versus dense bed region (bottom)
  - Inconsistency of particle contact in top results in unstable and inefficient heat transfer
  - Bottom of bed has higher heat transfer coefficient and yields more stable temperatures
  - PDU tests include both top and bottom locations for validation
- Parametric studies of heat removal versus operating conditions



Heat removal near TOP of AR

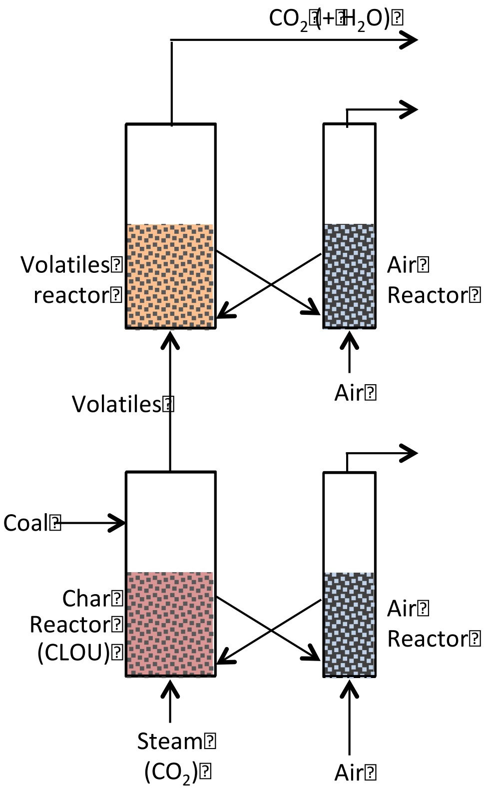


Heat removal near BOTTOM of AR

Technical Area 5:

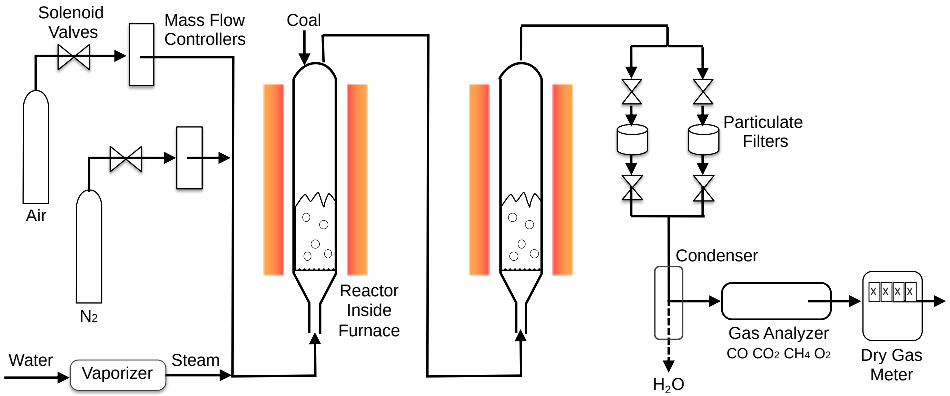
Evaluation of Novel Dual Bed/Dual Carrier CLC Reactor

- Objective: Investigate performance of alternative reactor for CLC and CLOU
- 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
  - Volatiles reactor
    - Situated above/downstream of char reactor
    - Use conventional low-cost CLC carrier to convert volatiles
  - Two oxygen carrier cycles and air reactors
- Approach
  - Reactor simulation and process modeling
  - Experimental evaluation in small fluidized beds



Dual-FR CLC Reactor Design Evaluation

- Computational modeling
  - Distribution of volatiles and char
  - Fuel conversion in CLOU reactor
  - Heat/energy analysis
- Experimental tests
  - Coupled fluidized bed reactors
  - Product gas from first reactor fluidizes second reactor
  - Batch tests with coal/coal char



Project Accomplishments

- Better understanding and predictability of oxygen carrier/ash interactions
  - Good agreement between models and experiments
- Effective separation of Cu from spent oxygen carrier
  - No reduction in oxygen carrier properties
  - Promising for minimizing loss and improving economics
- Improved operation of loop seals
  - Minimize premature O_2 release of CLOU carriers
- New disengager-based solid separation system developed
  - Separates OC from ash
- Improved chemical reactions in simulations
- Heat management/reactor temperature control scheme identified

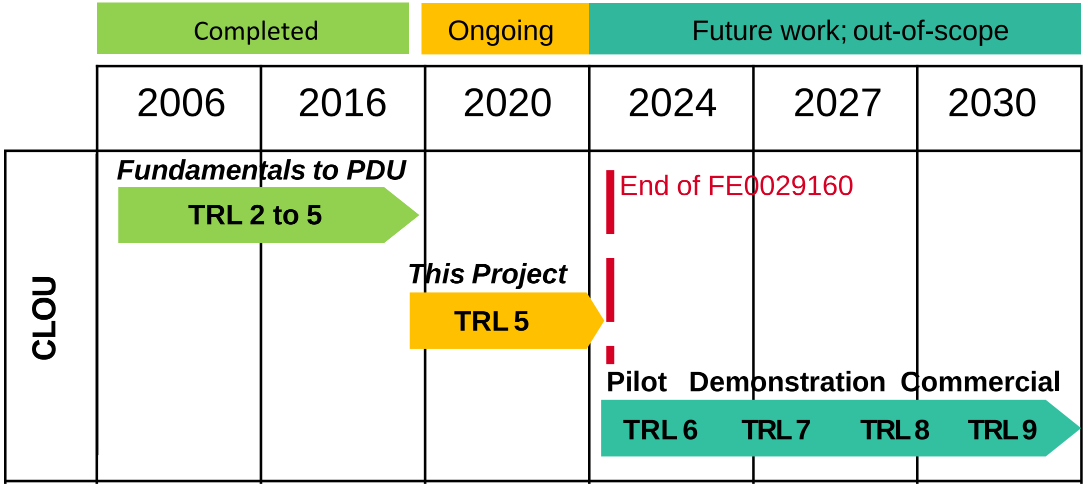
Supports DOE strategic goals

Attaining the Next TRL

- For Overall CLC / CLOU technology (to TRL 6)
  - More experience needed at PDU scale
    - Reliable startup and operating procedures
    - Stable, controllable operation
    - Ability to recover from upsets
    - Fail-proof temperature control
    - Long-term operation
  - Oxygen carrier development
    - Affordable
    - Able to be produced economically at large scale (> 10 tons)
    - Desirable properties (physically robust, reactive, high oxygen capacity, lifetime)
  - Strong economic motivation necessary
    - 45Q not sufficient
    - Requires government support for economic risk mitigation
    - Partner with Europe and China

Timeline for Technology Development

Fluidized Bed Chemical Looping Combustion



Wrap-Up

- 5 technical tasks aimed at improving performance/economics of CLC/CLOU
  - 3 of 5 tasks involve technology development

- Sub projects with new tech development increasing TRL
  - Oxygen carrier recycle: initial 2, current 3-4, project 4
  - Solids management: initial 2, current 3, project 4
  - Dual bed/carrier system: initial 2, current 3, project 4
  - → These address critical needs to improve competitiveness of CLC

- Fluidized bed CLC expected to remain at TRL 5 for several years
  - Much to be learned at industrially-relevant conditions
  - Operating hours, experience, troubleshooting, optimization needed
  - Need for large-scale, affordable oxygen carrier production
  - Need strong motivation for companies to invest in CO_2 capture