Overview of Chemical Looping Efforts at the National Energy Technology Laboratory

Doug Straub

NATIONAL ENERGY TECHNOLOGY LABORATORY

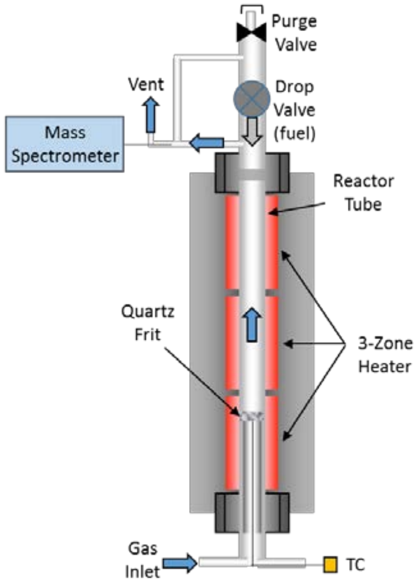
Oxy-Combustion and Chemical Looping Program Review, Pittsburgh, PA, August 25, 2017

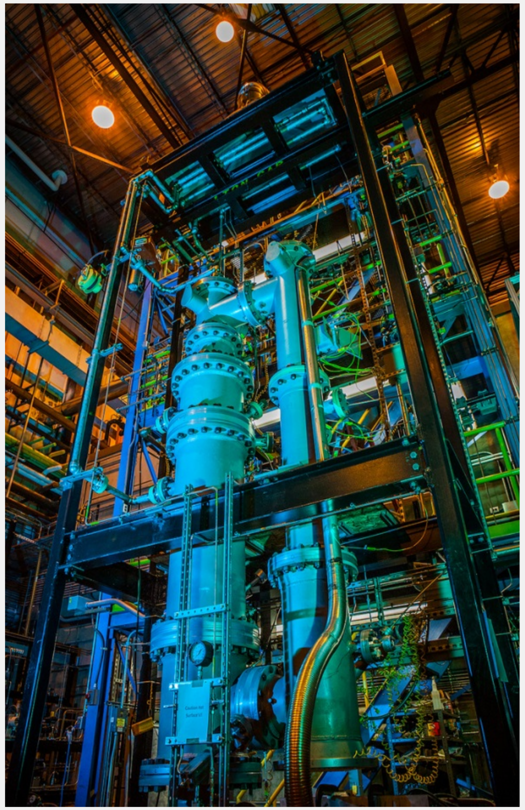
Solutions for Today | Options for Tomorrow

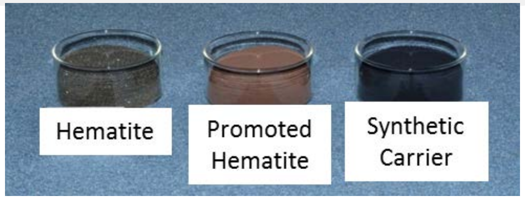
U.S. DEPARTMENT OF ENERGY

Outline

- **Motivation**
  - Purpose
  - Current status
  - Path forward
- **NETL/Research and Innovation Center (RIC) task breakdown for CLC**
- **Task by task description/summary**
- **Summary and conclusions**

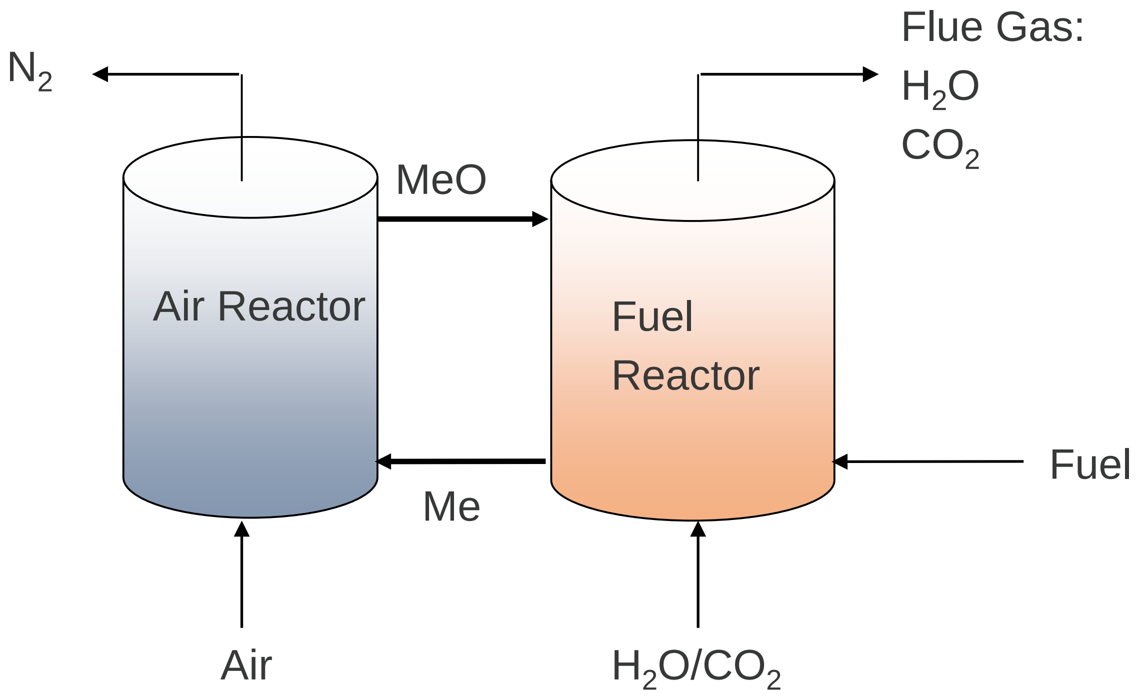






What Is Chemical Looping Combustion

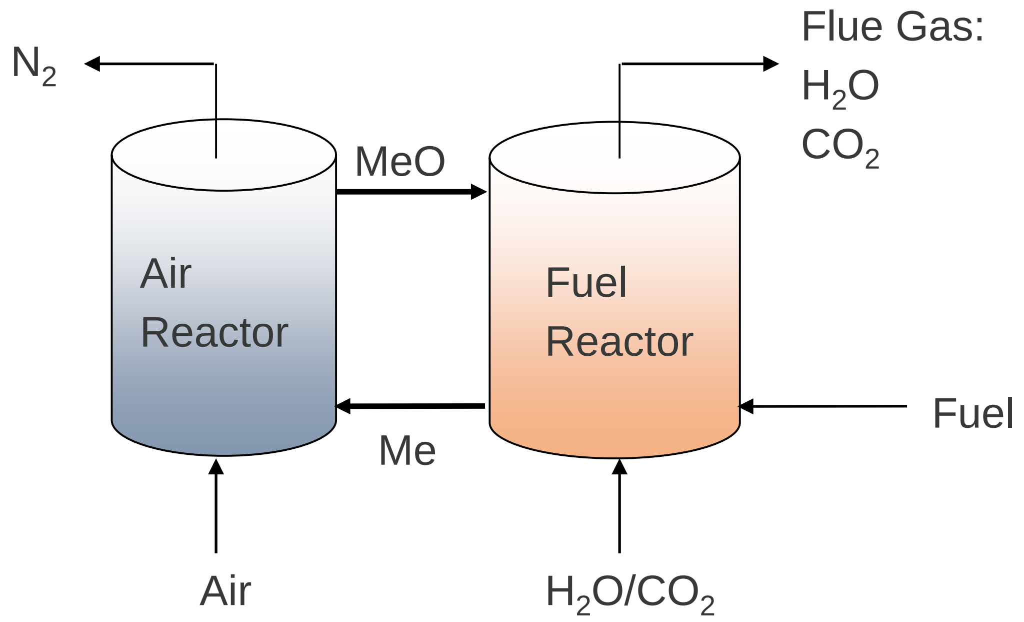
- **Fundamentally different approach to combustion**
  - Fuel and air do not mix
  - Oxygen transport is provided by solid O_2 carrier
- **CO_2 separation is as simple as condensing water vapor from flue gas (in theory)**
- **Typical temperature range (800-1000C)**
  - Too low for thermal NOx production
- **Capital equipment and process design is similar to CFB combustors**



Purpose

What is our end goal?

- **Determine if CLC is a feasible technology for FE and worthy of additional investment/development**
  - →Data and information for strategic decision making
- **If it is feasible, THEN**
  - Help developers overcome technical issues
  - Help technology be successful
  - Ultimate commercialization → produces jobs and growth



Where Are We Now?

Current Status

- **Preliminary techno-economic analyses (TEAs) have been completed** (DOE/NETL – 2014/1643)
    - Significant amount of uncertainty → very little proven reliable operating data
    - Operability and reliability are major challenges for technology feasibility
    - Oxygen carrier makeup costs are a key factor for circulating reactor systems
- **Technology gaps identified by developers**
- **CLC test facilities exist**
    - Operating experiences are limited to less than ~100 hrs
    - Data quality and reliability need improved
        - TEAs require proven reliable operating data

Exhibit ES-3 Cost of electricity breakdown comparison

Cost	Fe_2O_3 ($/MWh)	$CaSO_4$ ($/MWh)	Conventional PC BBR Case 12
Capital	49.6	53.4	73.1
Fixed	11.3	12.2	15.7
Variable	25.7	8.4	13.2
Maintenance materials	3.2	3.5	4.7
Water	0.4	0.4	0.9
Oxygen carrier makeup *	18.7	1.1	N/A
Other chemicals & catalyst	1.9	1.7	6.4
Waste disposal	1.4	1.7	1.3
Fuel	28.4	30.8	35.3
Total	115.1	104.7	137.3

*Fe_2O_3 oxygen carrier makeup: 132 tons/day @ $2,000 per ton; Limestone carrier makeup: 439 tons/day @ $33.5 per ton

Ref: DOE/NETL – 2014/1643 , Guidance for NETL's Oxycombustion R&D Program: Chemical Looping Combustion

How Do We Get There?

Critical issues that need to be addressed

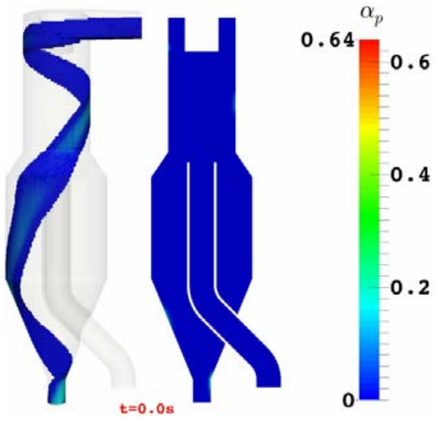
- **Determine if oxygen carrier make-up cost targets are feasible**
    - Establish a baseline
    - Execute strategy to achieve cost targets
- **More hours of continuous operation in small pilot-scale units**
    - Demonstrate steady-state operation
    - Confidence that components will meet performance requirements
- **Accelerate char conversion**
- **Determine if solid/solid separation for char and/or ash separation is feasible**

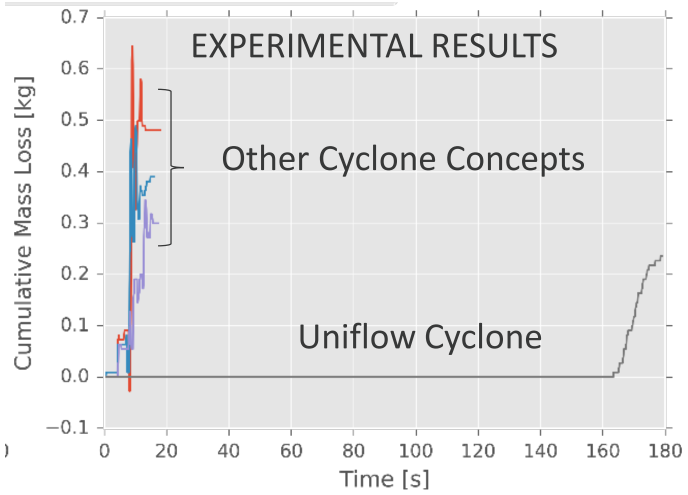
CLC Task Breakdown

- **Component development**
  - Achieve 80% separation of 1 wt% char in O_2 carrier at separation flux of 0.5 kg/m^2-s.
- **Carrier performance and durability**
  - Carrier make-up costs that are less than \$5/MW_{th}-hr.
- **Sensor development for CLC applications**
  - Demonstrate reliable solids circulation rate alternatives
- **Experimental testing and operations**
  - Demonstrate oxygen carrier make-up costs <\$5/MW_{th}-hr in a circulating CLC test facility
- **System Engineering and Analysis**
  - Develop research metrics and other research targets based on techno economic evaluations

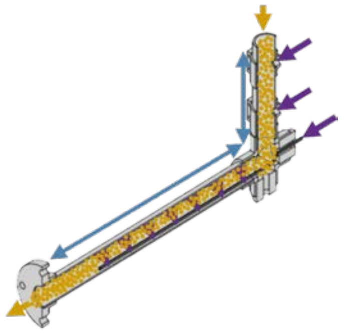
Component Development

- **Reduce Solids Losses During Process Upsets**
  - Metric: Order of magnitude lower solid loss rate relative to conventional cyclone

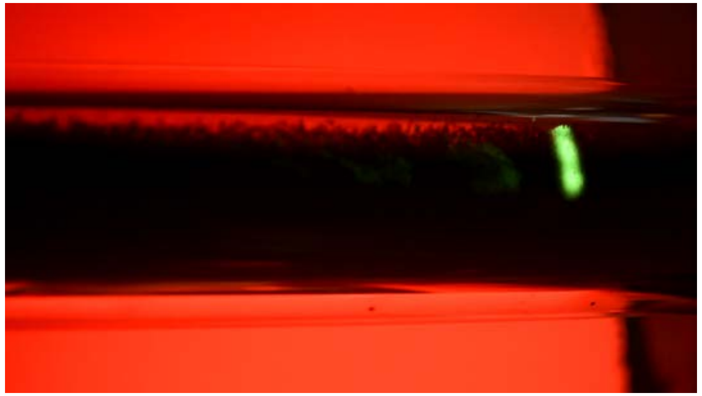




- **Improve Dense Horizontal Transport Performance Predictions**
  - Metric: Predict pressure drops to within 5% across an L-valve for CLC systems



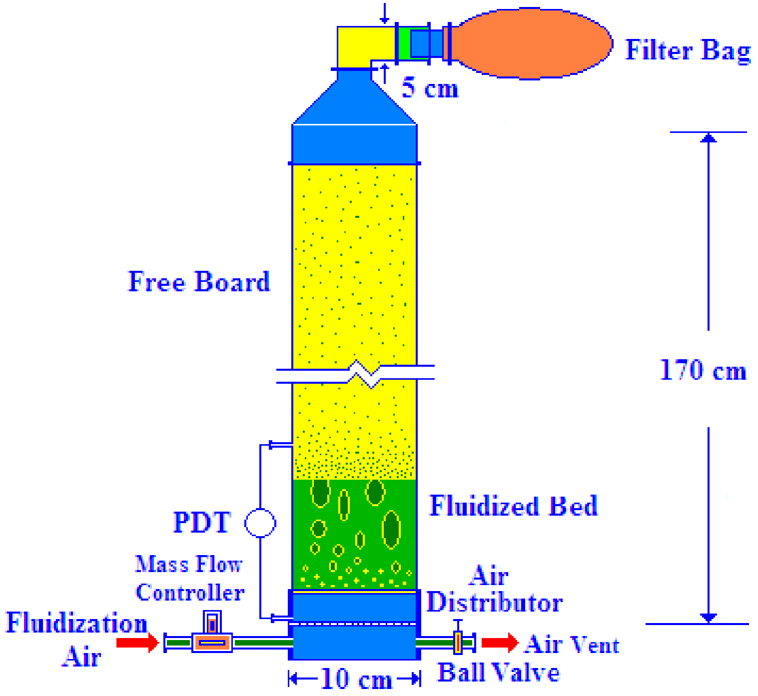
- **Solid-Solid Separations**
  - Metric: For less than 1 wt% char/carrier mixture, demonstrate 80% separation efficiency of fines and a separation flux of 0.5 kg/m^2-sec



Component Dev. – Solid-Solid Separations

For less than 1 wt% char/carrier mixture, demonstrate 80% separation efficiency of fines and a separation flux of 0.5 kg/m^2-sec

Material	Size Range (µm)				Sphericity	Density	U_t (m/s)	
	Max	Avg	Min	SMD*	(-)	(kg/m^3)	Largest	Smallest
Steel Shot	360	200	105	194.39	0.923	7890	X	1.78
Ilmenite	250	155	105	151.24	0.902	4457	X	1.24
Al_2O_3 (small)	500	309	149	293.97	0.821	3968	X	1.6
Al_2O_3 (large)	1000	613	300	550.56	0.820	3968	X	3.18
Glass Beads	123	93	37	75.3	0.912	2464	0.39	X



Correlation from Choi et al., 1985

$$K^*_{elu}\left(kg/m^2s\right) = 0.36(X_0)^{1.09}\left(\frac{U_g - U_t}{U_t}\right)^{3.83}$$

Correlation from Monazam et al., 2017

$$K^*_{elu}\left(kg/m^2s\right) = 0.354(X_0)^{1.366}\left(\frac{U_g}{U_t}\right)^{2.586}\left(\frac{\rho_{fine}}{\rho_{coarse}}\right)^{-0.444}$$

	Steel Shot / Glass Beads	Ilmenite / Glass Beads	1000x300µm Al_2O_3 / Glass Beads	500x149µm Al_2O_3 / Glass Beads
Static bed depth (cm)	7.62	7.62	7.62	7.62
Aspect Ratio, L/D (-)	0.75	0.75	0.75	0.75
Dimensionless velocity, U_g/U_{t_gb} (-)	0.8, 1.0, 1.2	0.8, 1.0, 1.2	1.0, 1.2, 1.5, 1.8, 2.0, 2.2, 2.5, 3.0	1.0, 1.2, 1.5, 2.0, 2.5, 3.0
Gas Velocities (m/s)	0.31, 0.39, 0.47	0.31, 0.39, 0.47	0.39, 0.47, 0.59, 0.70, 0.78, 0.86, 0.98, 1.17	0.39, 0.47, 0.59, 0.78, 0.98, 1.17
Percentage of Glass Beads (wt%)	57	57	2, 25, 57, 77	2, 25, 57, 77, 95

Requires extrapolation to less than 1 wt% fines

Ref: Monazam, Breault, Weber, and Mayfield, “Elutriation of fines from binary particle mixtures in bubbling fluidized bed cold model,” *Powder Technology* (2017), pp. 340–346

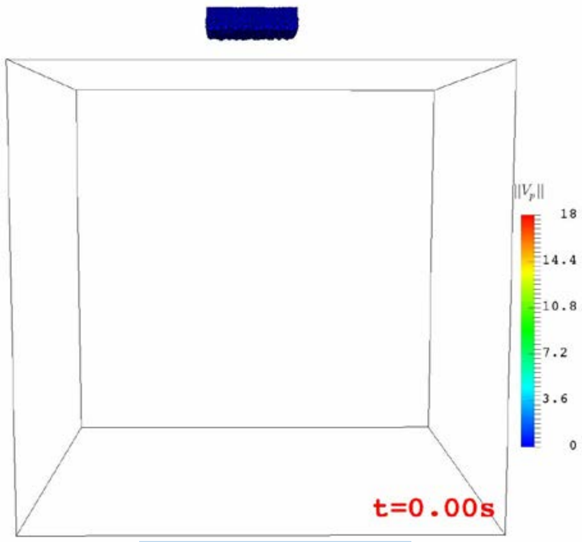
Component Dev – Solid-Solid Mixing

Scoping study to provide fundamental understanding of solid-solid mixing and investigate feasibility to develop CLC reactor design tools

Material

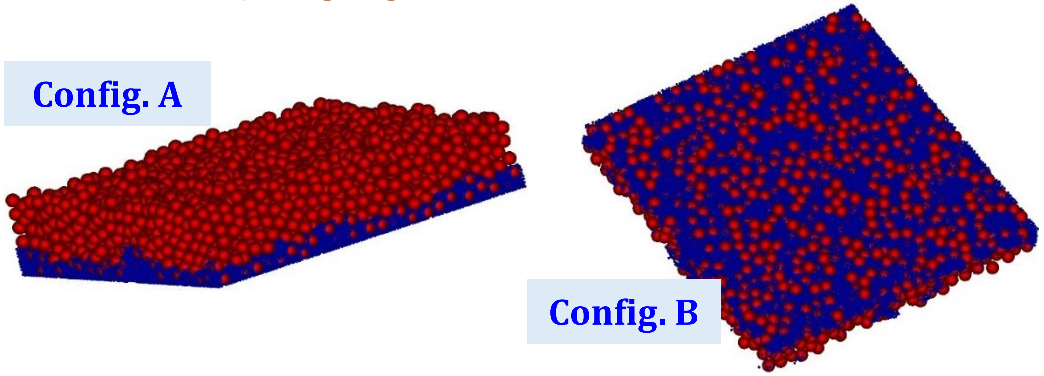
	Diameter [μm]	Density [kg/m³]
Coal	200	1000
Ash	40	2650
Oxygen Carrier (D)	1500	2500

Ash content (% mass)= {15, 25, 50, 75}



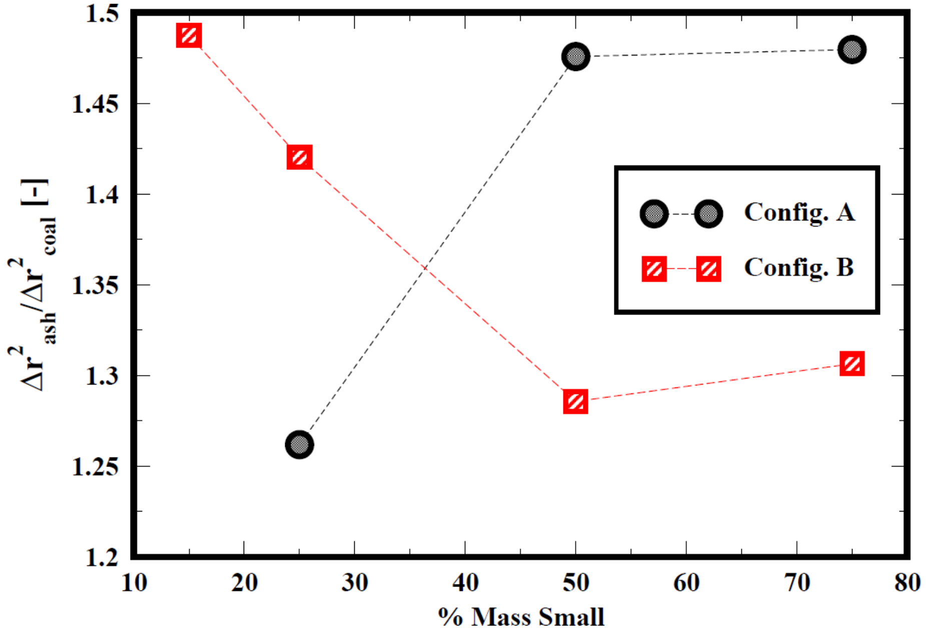
Config. B
75% ash -

Fully Segregated Binary Mixture



25% ash (Red: coal and Blue: ash)

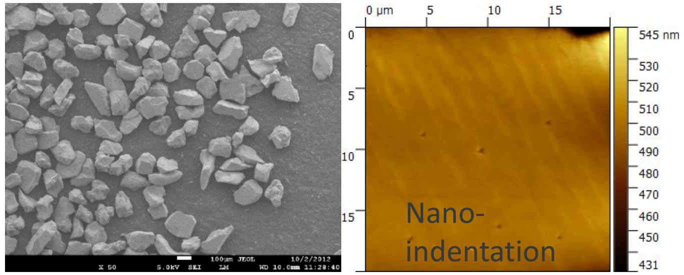
➔ Wider dispersion of smaller particles

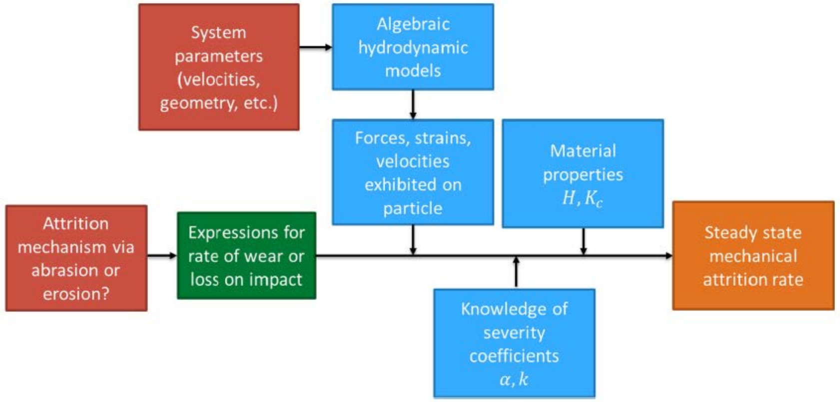


O_2 Carrier Performance and Durability

Metric: O_2 carrier make-up cost performance should be less than \$5/MW_{th}-hr

- **Carrier Manufacturing**
  - Develop and manage interactions with external manufacturers
- **Attrition Studies**
  - Develop engineering model for attrition based on first principles
- **Metallurgical Surface Degradation**
  - Improve oxygen carrier microstructural changes to redox reactions
- **Novel Oxygen Carrier Scoping Studies**
  - Higher temperature oxygen carrier materials (i.e., 1100-1200°C)
    - Faster char gasification → Better fuel conversion? → No char/carrier separation?
  - High oxygen transport capacity oxygen carriers (i.e., oxygen transport capacities in excess of 10 wt%).
    - Higher oxygen/carrier ratio → Lower circulation rate? → Lower make-up rate?
  - CLOU scoping studies

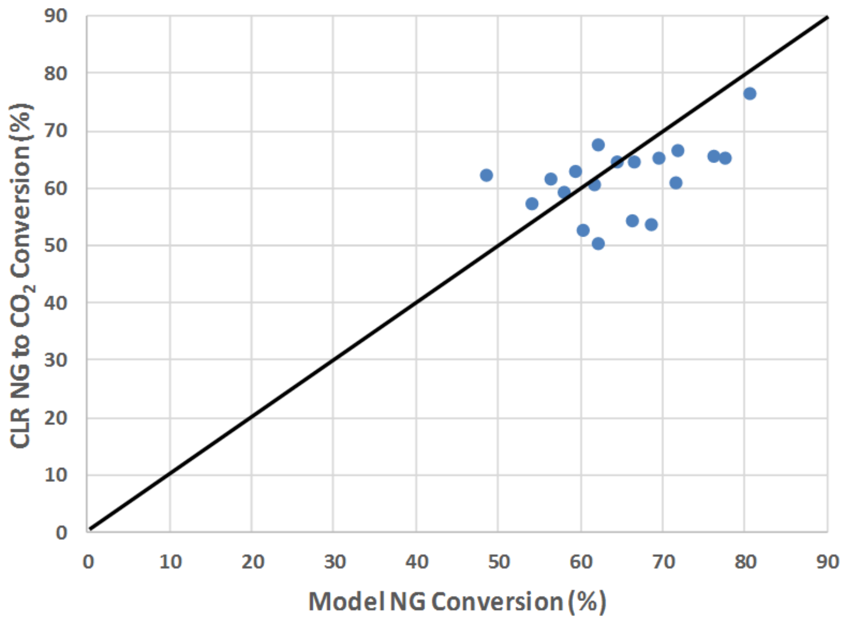




Systems Engineering and Analysis

Develop research metrics and other research targets based on techno-economic evaluations

- **NETL fluidized bed fuel reactor models validated using 50 kW_{th} CLR data**
  - Improves confidence and accuracy of CLC plant level TEA models
  - Provide R&D guidance to future CLR test operation
- **Initial phase of NETL study on generalized oxygen carrier types**
  - Higher temperature circulating CLC reactor (iron-based)
  - Higher oxygen transport capacity circulating CLC reactor (iron-based)
  - CLOU oxygen carrier analysis (copper-based carrier)

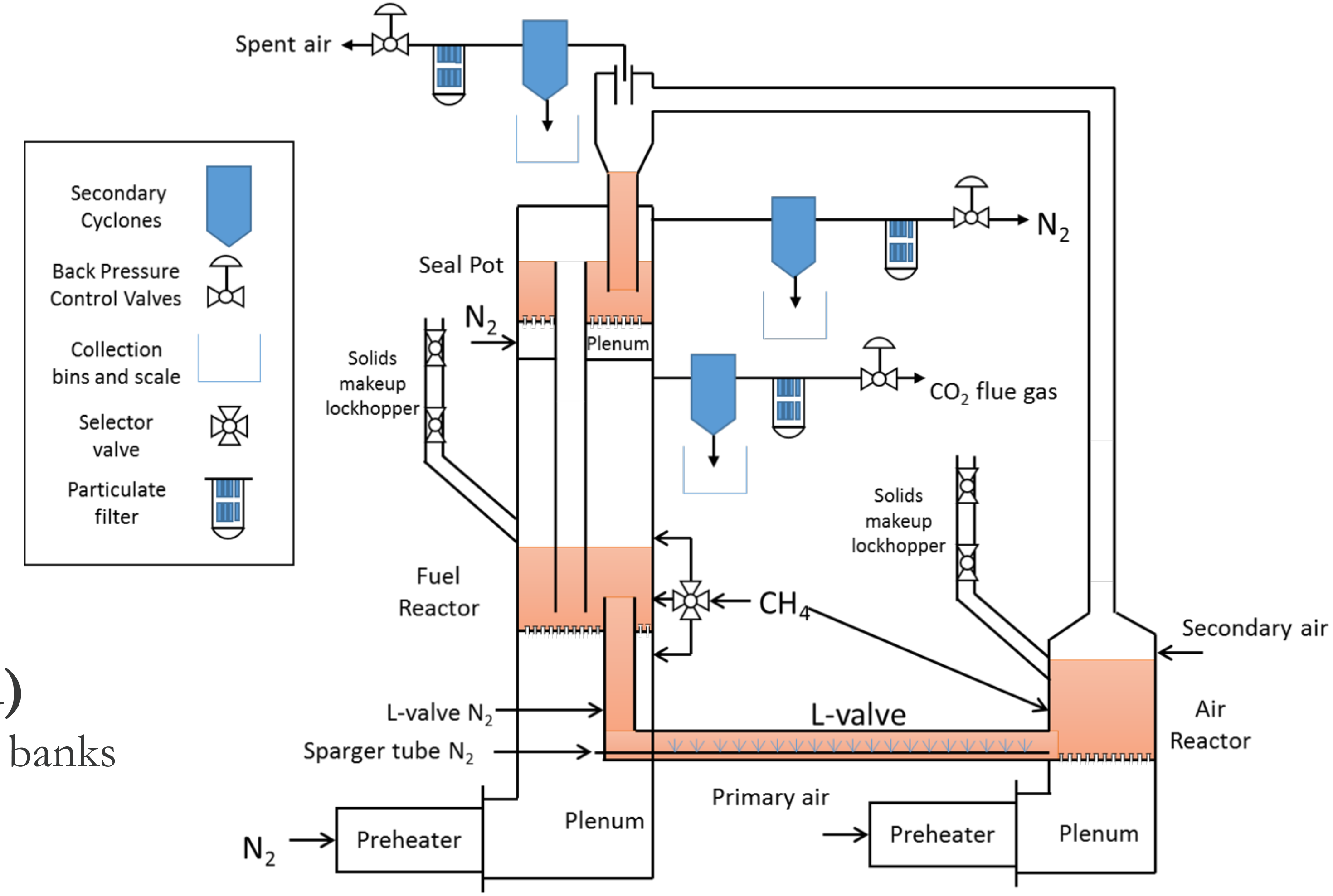


Ref: R. Stevens, R. Newby, D. Keairns, and M. Woods, "Chemical Looping Combustion Reference Plant Design And Sensitivity Studies Using NETL's Oxygen Carrier", (2017), Clearwater Clean Energy Conference, June 11-15, 2017

NETL 50 kW_{th} Circulating CLC Testing

Test Setup

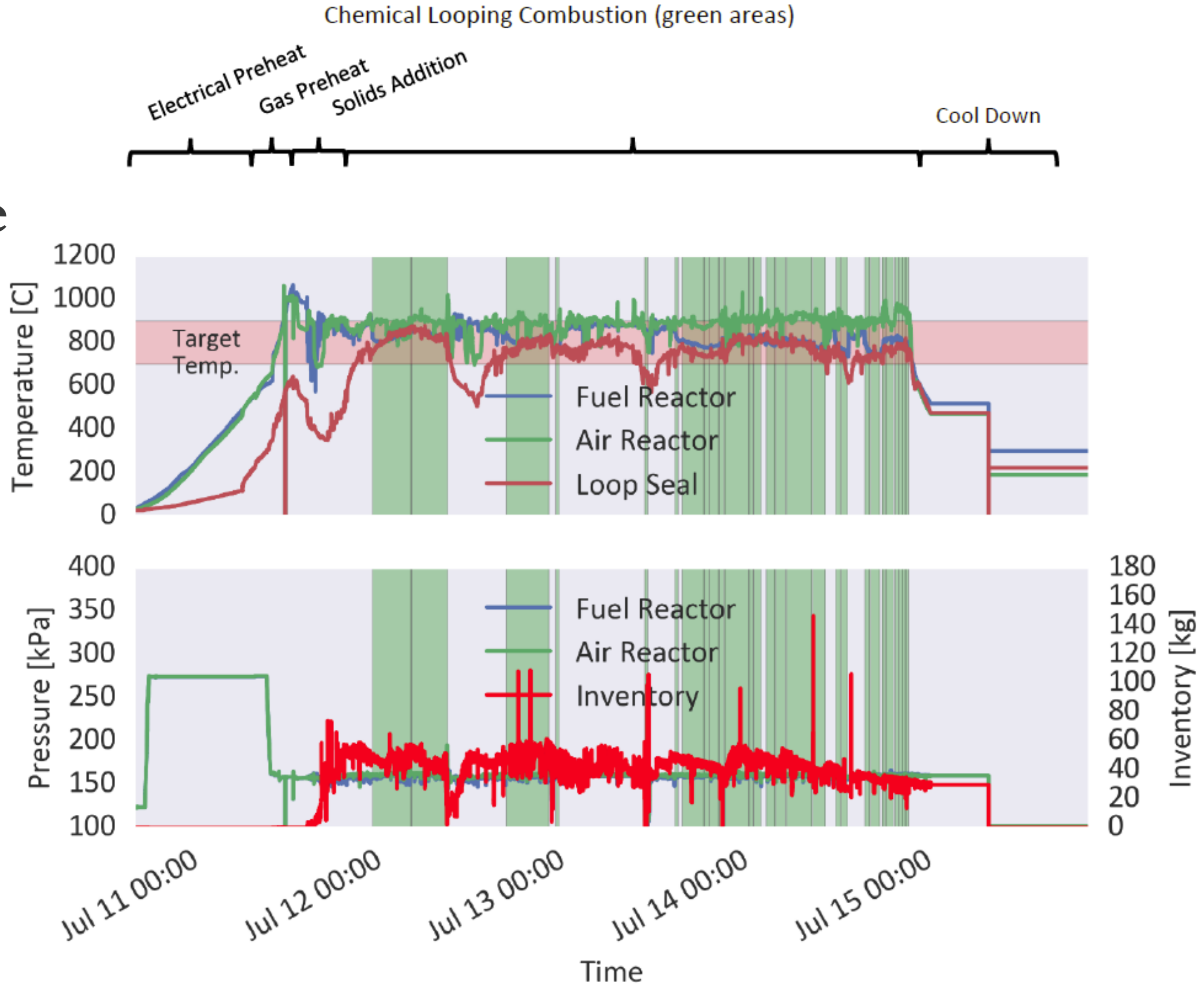
- **Carbon steel shell/refractory lined**
- **Fuel Reactor**
  - Bubbling bed (8” dia)
  - Natural gas (1 of 3 locations)
- **Air Reactor**
  - Turbulent fluidized bed (6” dia)
  - Natural gas for startup
- **Gas Seal/Seal Pot**
  - Bubbling bed (8” dia)
- **Vent lines (3 individually controlled)**
  - Cyclones remove hot solids prior to filter banks
  - Back-pressure control valves



NETL 50 kW_{th} Circulating CLC Testing

Recent Summary of Test Results

- NETL patented Cu/Fe/alumina (2nd Gen)
- 3.3 days of circulation in target temp range
- Accumulated 40 hours of CLC operation
  - Temperature ranges
    - Fuel Reactor – (760-815°C)
    - Air Reactor – (840-915°C)
  - Circulation rate (100-200 kg/hr)
  - Fuel conversion (50-80%)
  - Carbon balance (95-100%)
- O_2 carrier losses during CLC operation
  - New carrier was used for make-up



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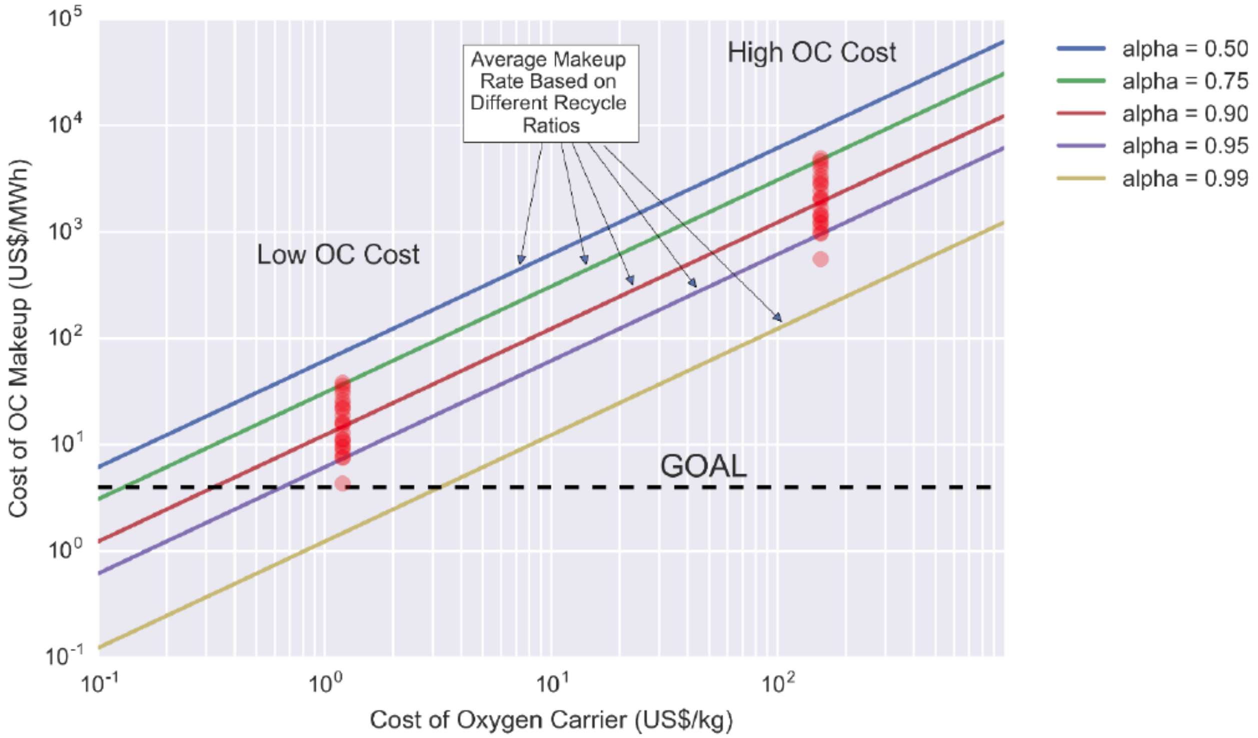
NETL 50 kW_{th} Circulating CLC Testing

Demonstrate oxygen carrier make-up costs \$5/MW_{th}-hr in a circulating CLC test facility

- **O_2 carrier make-up costs**
  - Baseline for 50kW_{th} test unit estimated
  - Key issue for CLC technology maturation
- **Gaps to address . . .**
  - Lower-cost O_2 carriers
  - Fundamental effects of redox cycling on attrition
  - Need longer duration tests under redox and circulating conditions
- **More studies are needed**



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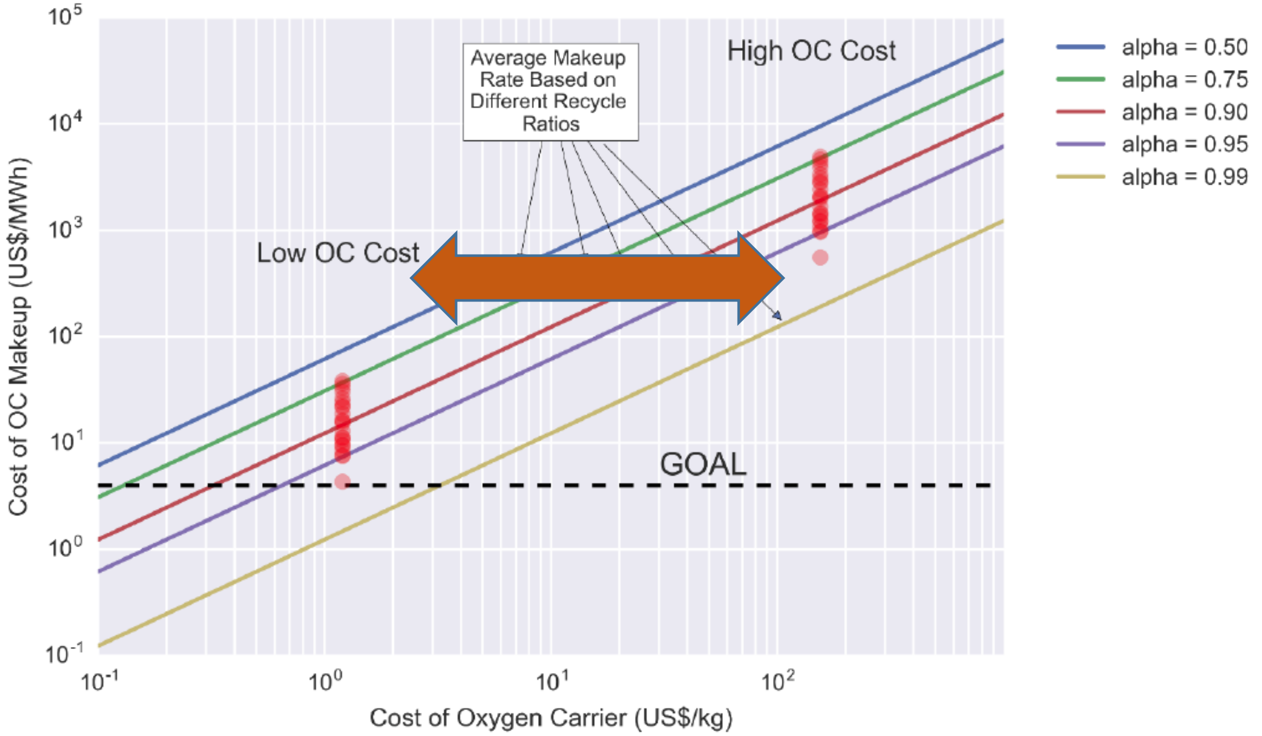
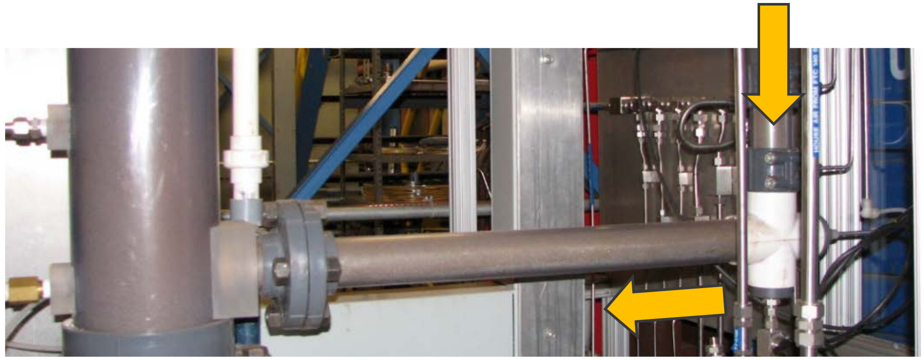
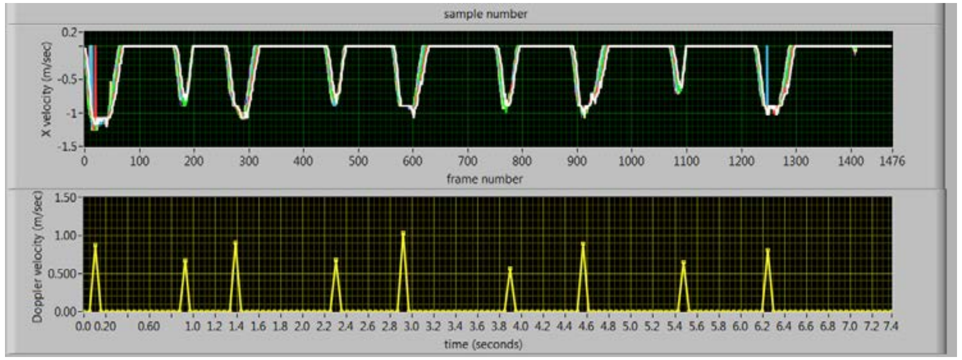


Sensor Development For CLC Applications

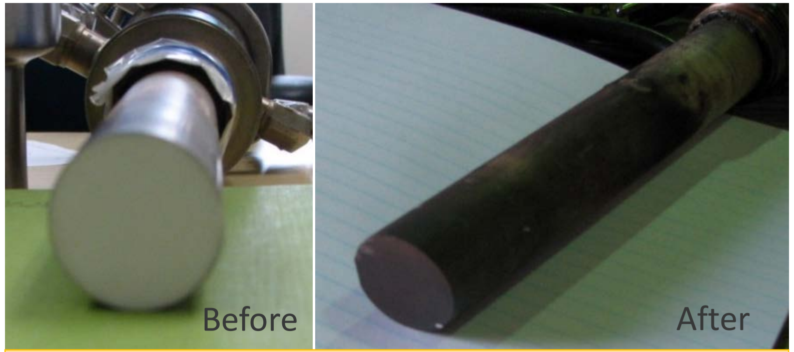
Demonstrate reliable O_2 carrier circulation rate alternatives

- **Microwave doppler sensor concept**
  - Developed for high temperature applications
  - Tested in NETL's Chemical Looping Reactor
- **Second generation sensor design in progress**
  - Addresses coating issues in hot tests





Microwave sensor detects mean particle velocities in L-valve (cold flow testing)



Conductive deposits on the alumina waveguide reduces signal

Ref: B. Chorpening, M. Spencer, R.C. Stehle, J. Charley, and D. Greve "Doppler Sensing of Unsteady Dense Particulate Flows", (2016), IEEE Sensors

Summary and Conclusions

- **CLC is a promising approach for cost effect CO_2 capture**
  - Projected capital cost is comparable to Circulating Fluidized Bed (CFB) combustion systems
  - Operating cost is still area of concern → reliable operating data is needed
- **Summary of recent accomplishments for NETL/RIC**
  - NETL bubbling fluidized bed fuel reactor model validated using 50 kW_{th} NETL test data
    - Improves confidence and accuracy of CLC plant level TEA models
  - Demonstrated NETL's patented high O_2 capacity carrier
    - Reduces solids circulation rate requirement → lower OC make-up cost
    - New low cost manufacturing approach used by commercial vendor
    - 40 hours of CLC operation/1.6 hours of auto-thermal operation (i.e., no auxiliary heat addition)
  - Scoping studies in progress (solid-solid mixing, high temperature OC's, char/carrier separation, etc.)