Operation of a 50-kw Chemical Looping Combustion Test Facility Under Autothermal Conditions

NATIONAL ENERGY TECHNOLOGY LABORATORY

Sam Bayham, Doug Straub, Justin Weber

Thermal Science Team, Research & Innovation Center

Chemical Looping at NETL

Component Development

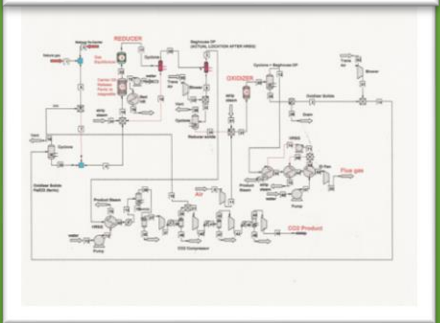
- Experimental (cold models)
- Simulations (MFIX, Barracuda)

Chemical Looping Reactor

System Studies

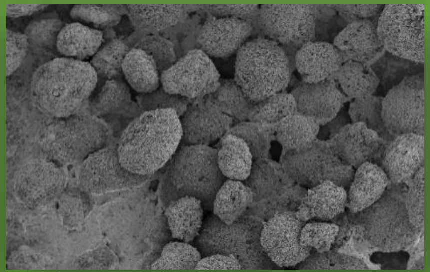
Cost	Fe_2O_3 ($/MWh)	$CaSO_4$ ($/MWh)	Conventional PC BBR Case 12
Capital	49.6	53.4	73.1
Fixed	11.3	12.2	15.7
Variable	25.7	8.4	13.2
Maintenance materials	3.2	3.5	4.7
Water	0.4	0.4	0.9
Oxygen carrier makeup *	18.7	1.1	N/A
Other chemicals & catalyst	1.9	1.7	6.4
Waste disposal	1.4	1.7	1.3
Fuel	28.4	30.8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

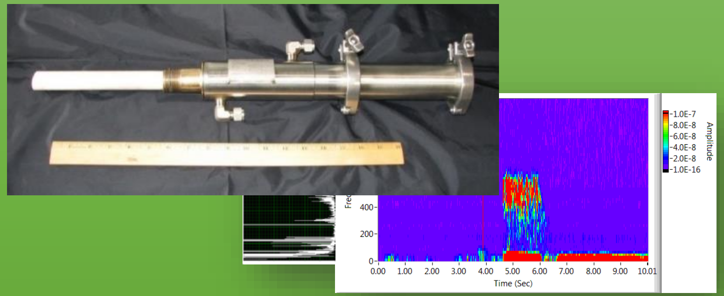


Oxygen Carrier Performance and Durability

- Reactivity
- Strength/Attr.
- Characterization



Sensor Development

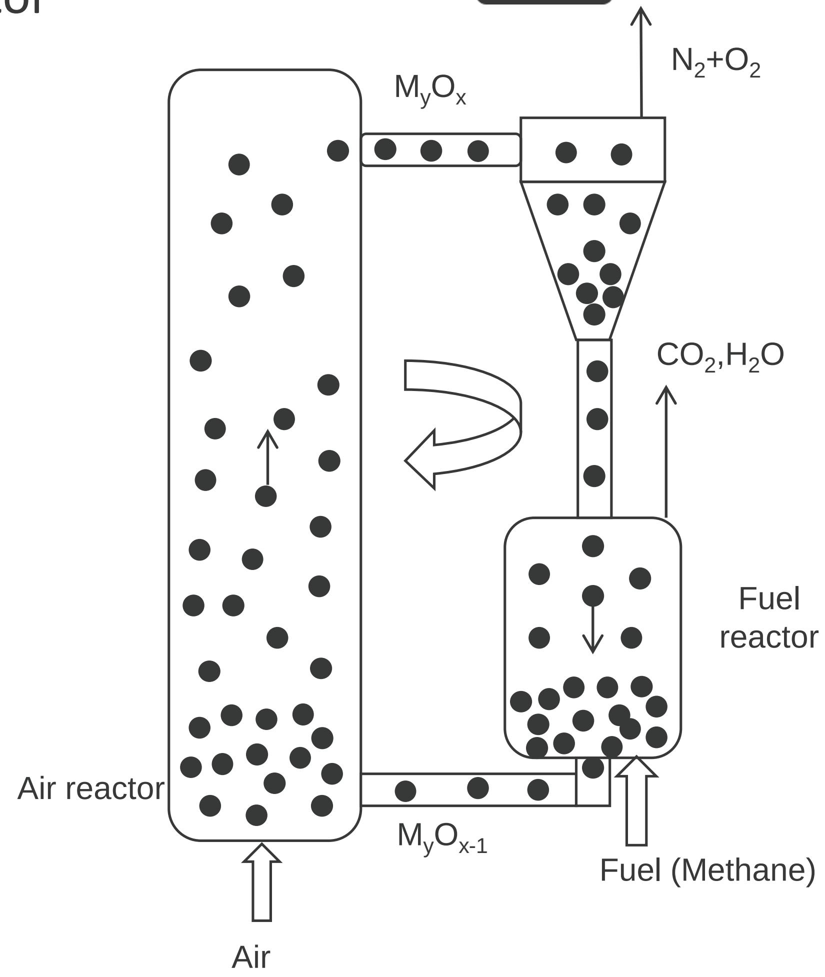


- Gas composition
- Solids flowrate

Key Challenges for CLC

- Paper studies have shown carrier makeup cost to be the greatest factor in CLC plant economics[1]
  - **Makeup cost = OC Cost times Makeup Rate**
  - **Makeup rate** dependent on metal oxide **attrition** rate

Sensitivity Parameter[1]	Cost of Steam
Oxygen carrier reactivity (relative to reference system)	Small -
Oxygen carrier loss (0 %) and price ($0/lb)	Large +
Oxygen carrier size (0.35mm) and density (203 #/cf)	Small -
Oxygen carrier conversion (from reducer 53%; from oxidizer 95%)	Small +
Reactor temperature (1700 °F)	Small -
Reactor velocities (reducer outlet 32 ft/s, oxidizer outlet, 29 ft/s)	Small +
Natural gas conversion (97.5%)	Small +
Oxidizer excess O2 (3.6 mol% in off-gas)	Small +

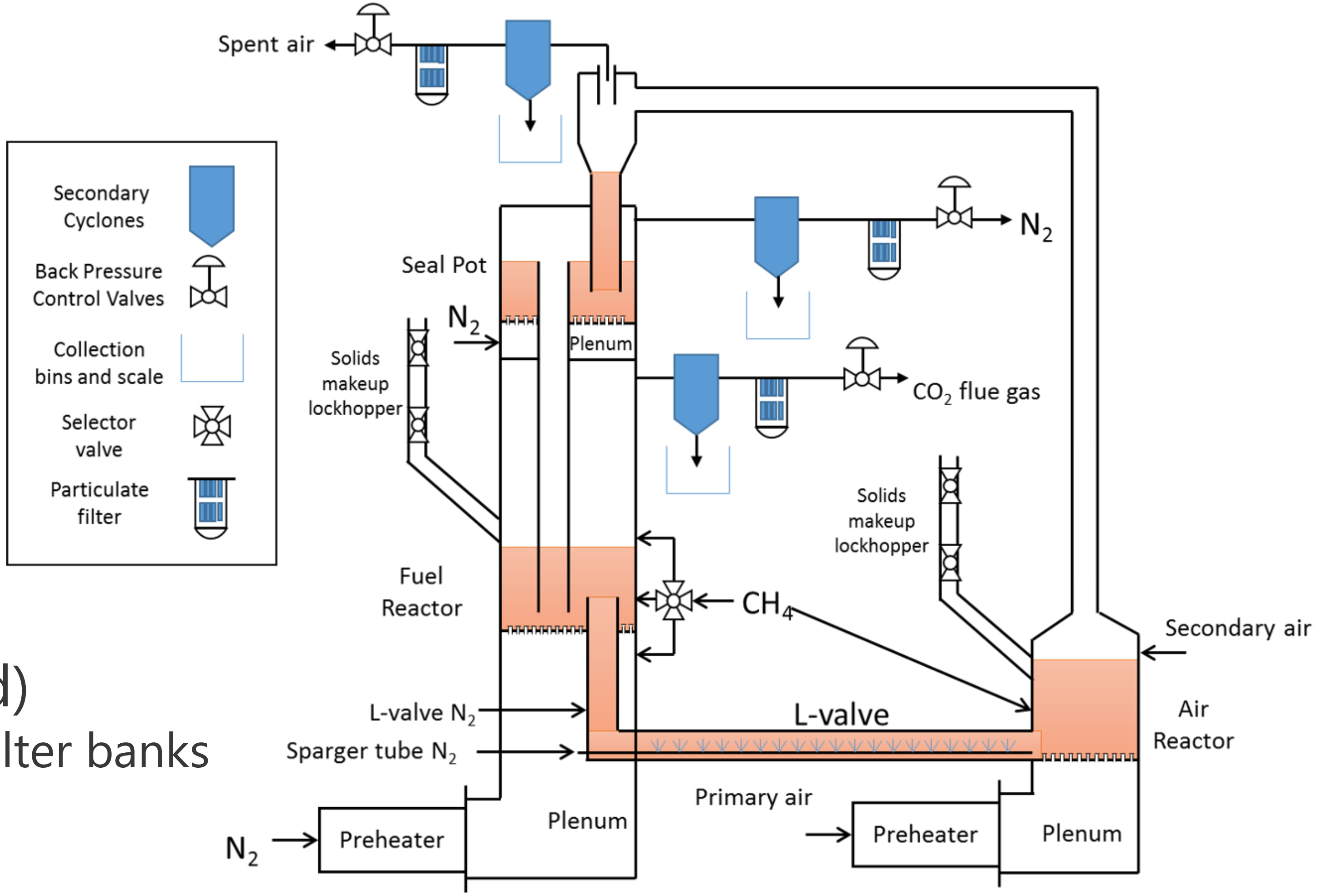


[1]"ICMI CLC Techno-Economic Study with CLC Reactor Modeling." Report number URS-RES-1-1109, November 2014.

Experimental testing and operations

NETL 50 kW_{th} Circulating CLC Testing

- 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



Ref: Bayham, S., Straub, D., and Weber, J., (2017), "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," https://www.osti.gov/scitech/biblio/1347568-operation-netl-chemical-looping-reactor-natural-gas-novel-copper-iron-material

Carriers tested in CLR

	Hematite	Promoted Hematite	Synthetic Carrier	
Particle density	4.9	4.9	2.9	g/cm3
Sauter Mean Diam.	210	210	343	µm
D50	238	238	397	µm
Sphericity	0.876	0.876	0.91	--
Umf (at 298 K)	8.55	8.55	14	cm/s
Fe_2O_3	86.6%		31%	
CuO			37%	
“Inert”	13.4%		31%	

- Bi-metallic carrier (CuO and Fe_2O_3) with alumina
- High reactivity (compared to raw hematite)
- Reduction of material with CH_4 is slightly exothermic.
- Scaled up to ~400 lb batch by Nextech

[Siriwardane, R.; Tian, H.; Simonyi, T.; Poston, J. (2013) Synergetic effects of mixed copper–iron oxides oxygen carriers in chemical looping combustion. *Fuel* **108**, 319-333.

[Siriwardane, R.; Tian, H.; Miller, D.; Richards, G. (2015) Fluidized bed testing of commercially prepared MgO-promoted hematite and CuO–Fe2O3 mixed metal oxide oxygen carriers for methane and coal chemical looping combustion. *Applied Energy* **157**, 348-357.

Ref: Bayham, S., Straub, D., and Weber, J., (2017), “Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material,” https://www.osti.gov/scitech/biblio/1347568-operation-netl-chemical-looping-reactor-natural-gas-novel-copper-iron-material

Original Test Plan

Test Condition		Natural Gas Only				
		TC-03	TC-04	TC-05	TC-06	TC-07
Pressure	psig	8	8	8	8	8
Heating Value	kWth	10	20	30	40	50
Fuel Reactor Temperature*	°F	1550	1550	1550	1550	1550
Flows into FR						
Nat. gas FR (FIC-325)	scfh	32	68	102	136	171
Nitrogen FR (FIC-525)	scfh	397	361	327	293	259
Steam FR (FIC-407)	lb/hr	0	0	0	0	0
Flows into AR						
Primary Air (FIC-165)	scfh	500	500	500	500	500
Secondary Air (FIC-125)	scfh	1400	1400	1400	1400	1400

*Difficult to control and will depend on extent of reduction reaction

Main Goals:

- Long autothermal trials reusing ejected solids for makeup

Conditions:

- Constant FR velocity (0.276 m/s) but changes in methane concentration
- Attempt to set FR temp to 1550 °F
- Solids Inventory: 100 lb (kept constant through run)

Performance Parameters Measured

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1. Carbon Balance

$$C_{\text{bal}} = \frac{\dot{N}_{\text{CH}_4\text{,out}} + \dot{N}_{\text{CO}_2\text{,out}} + \dot{N}_{\text{CO,out}}}{\dot{N}_{\text{CH}_4\text{,in}}}$$

"Sanity check", and to determine if major fuel reactor gas leakage

2. Methane Conversion

Measured two ways:

$$X_{\text{CH}_4} = \frac{\dot{N}_{\text{CH}_4\text{,in}} - \dot{N}_{\text{CH}_4\text{,out}}}{\dot{N}_{\text{CH}_4\text{,in}}}$$

Overall conversion

$$X_{\text{CH}_4 \rightarrow \text{CO}_2} = \frac{\dot{N}_{\text{CO}_2\text{,out}}}{\dot{N}_{\text{CH}_4\text{,in}}}$$

Conversion to CO_2

If a significant fraction of fuel is converted to CO or carbon, instead of CO_2, then the first approach would bias the calculated conversion toward higher values than the second approach.

3. Oxygen Carrier Conversion

$$X_{OC} = \frac{\dot{N}_{\text{O,out}}}{\dot{N}_{\text{O,total}}}$$

$$\dot{N}_{\text{O,out}} = \dot{N}_{\text{H}_2\text{O,out}} + 2\dot{N}_{\text{CO}_2\text{,out}} + \dot{N}_{\text{CO,out}}$$

$$\dot{N}_{\text{O,total}} = \dot{m}_{\text{OC}} \left(\frac{3 f_{\text{Fe}_2\text{O}_3}}{MW_{\text{Fe}_2\text{O}_3}} + \frac{f_{\text{CuO}}}{MW_{\text{CuO}}} \right)$$

Determines how many moles of oxygen are being extracted over the theoretical maximum

4. Gas and Solid Residence Times

$$\tau_{\text{g,FR}} = \frac{h_{\text{bed,FR}}}{U_{\text{g,LM}}}$$

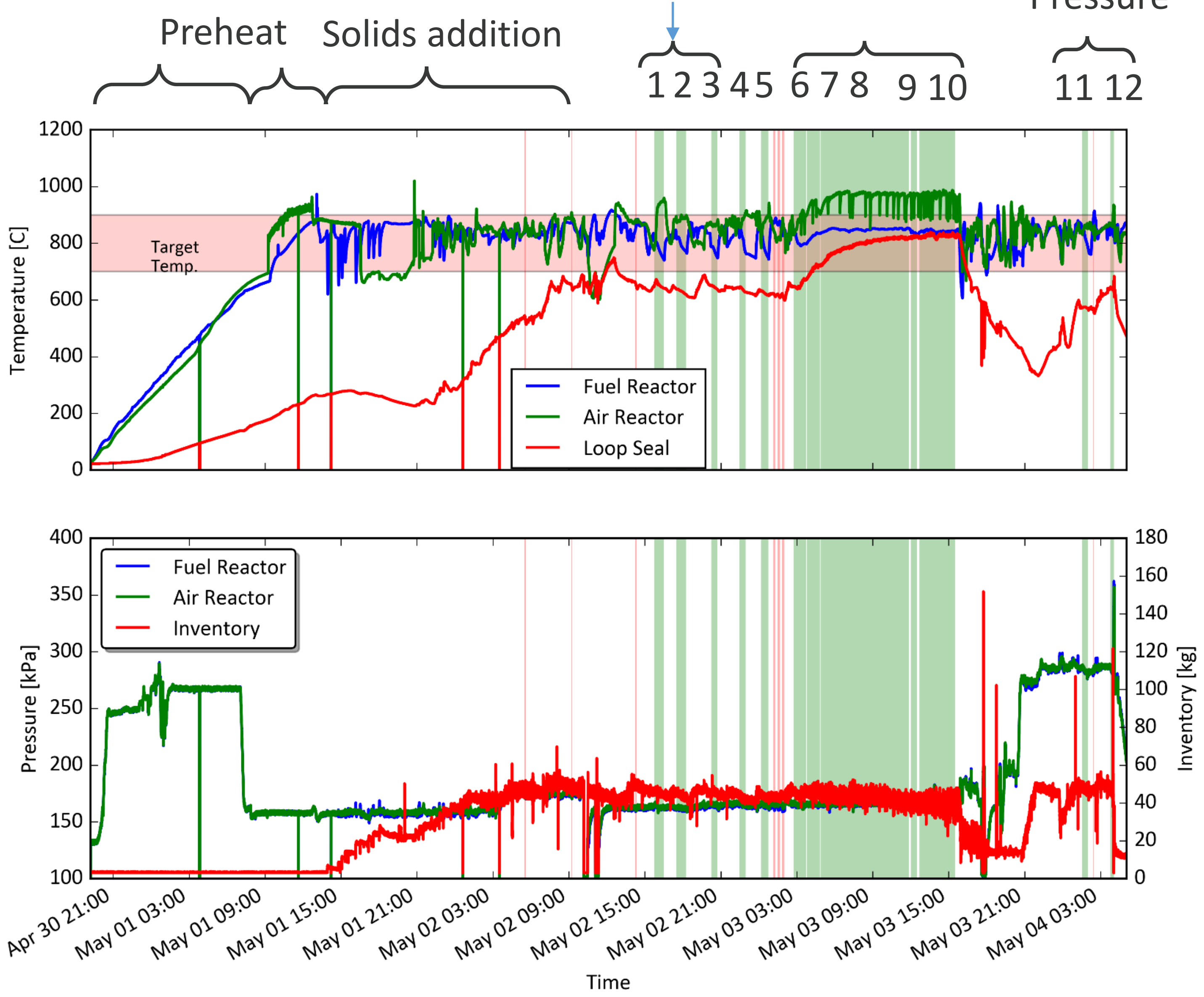
Determined from log-mean flowrate

$$Q_{\text{LM}} = \frac{Q_{\text{T,wet}} - Q_{\text{in}}}{\ln\left(\frac{Q_{\text{T,wet}}}{Q_{\text{in}}}\right)}$$

$$\tau_{\text{OC,FR}} = \frac{m_{\text{bed,FR}}}{\dot{m}_{\text{OC}}}$$

**Important parameters for how long it takes fuel to react with oxygen carrier.

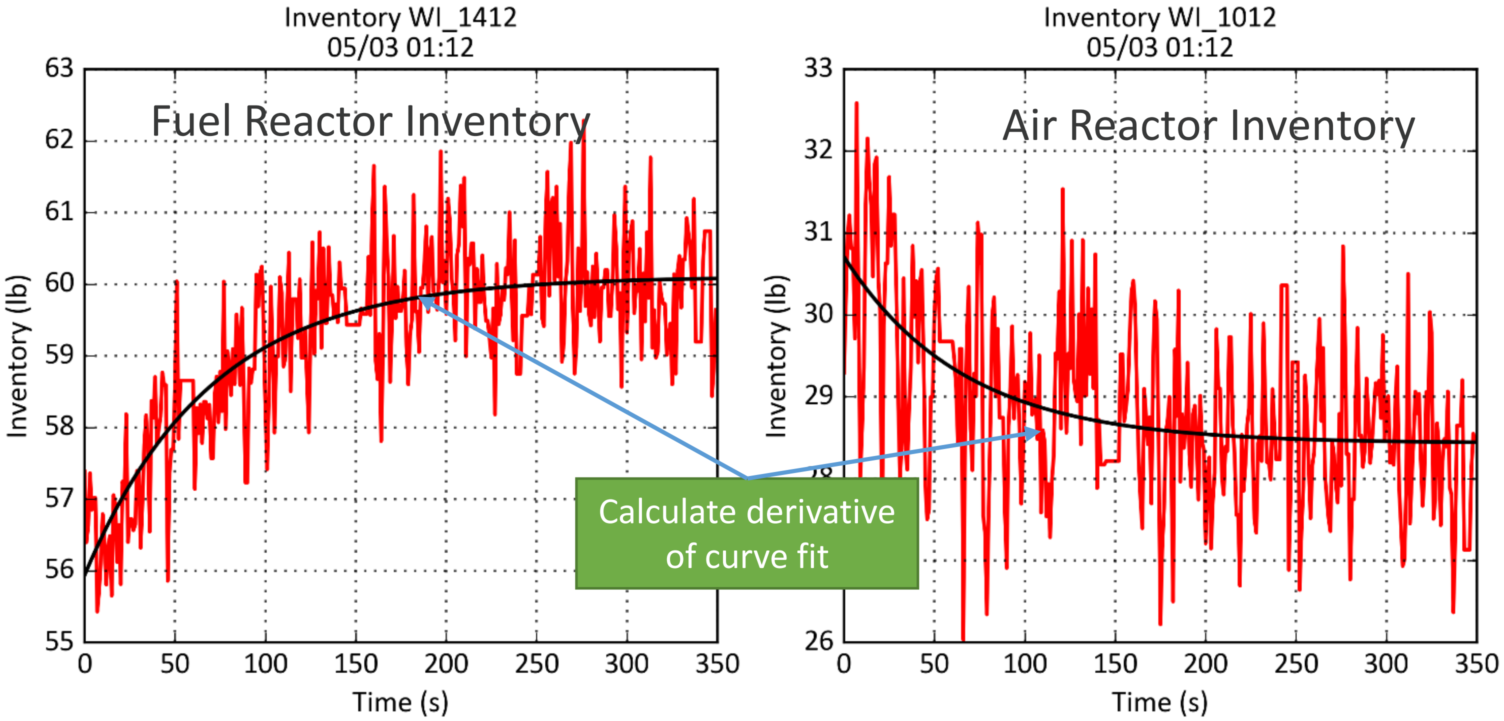
Summary Slide



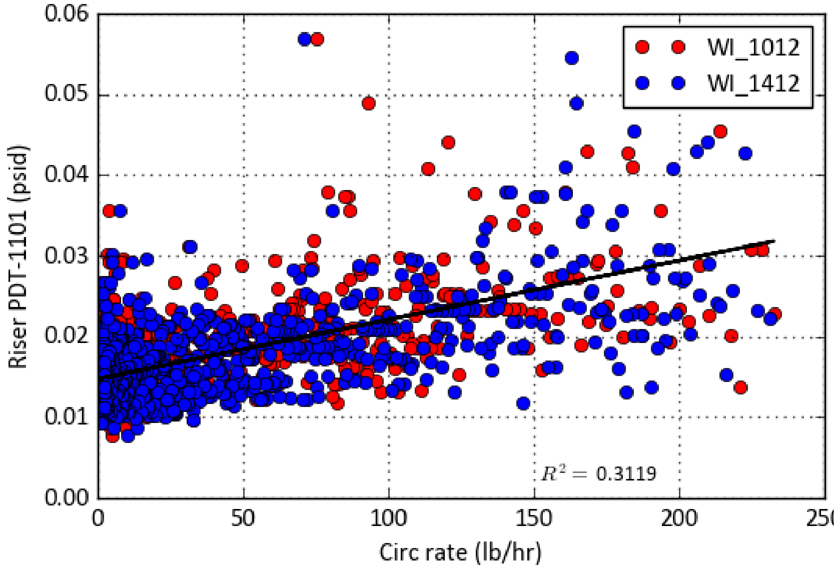
- Electric preheat
  - Room temperature → Auto-ignition temperature
- Natural gas augmented preheat
  - 1200°F to 1800°F
  - Gas phase combustion in both reactors
- Carrier addition
  - Reduce gas flows
  - Add carrier in batches via lockhopper
- Chemical looping combustion
  - Transition from air to N2 as fluidizing gas in FR
  - Adjust natural gas flow for CLC

L-Valve Cutoff Tests

- Shut off L-valve and solids flow to observe change in inventory in air and fuel reactors
- Fit pressure drop data
- Cutoffs performed before autothermal
- FR Backpressure controller was set to zero during cutoff test
  - This allowed for solids to stop circulating, since we were running it higher than usual



Riser DP Correlation



Riser pressure as a function of riser DP

$$\dot{m}\left[\frac{\text{kg}}{\text{h}}\right] = 6187 \cdot \Delta P_{\text{riser}}[\text{psid}] - 91.19$$

Autothermal trials

11 hours of autothermal with CuFe material performed with recycled solids!

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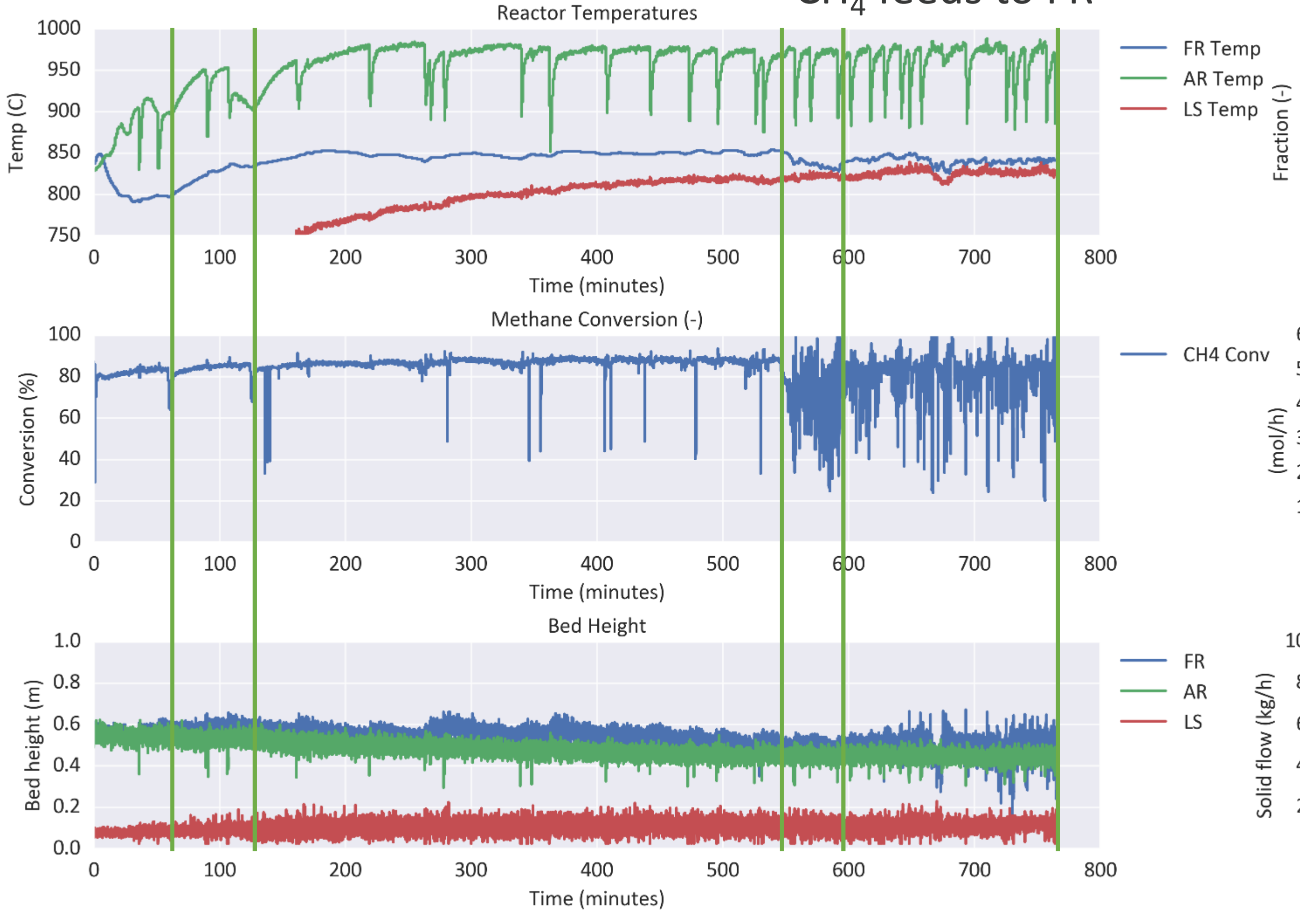
Trials TC-05,-06,-07

TC-05 -06 TC-07

50% and 45% CH_4 feeds to FR



TC-05 -06 TC-07

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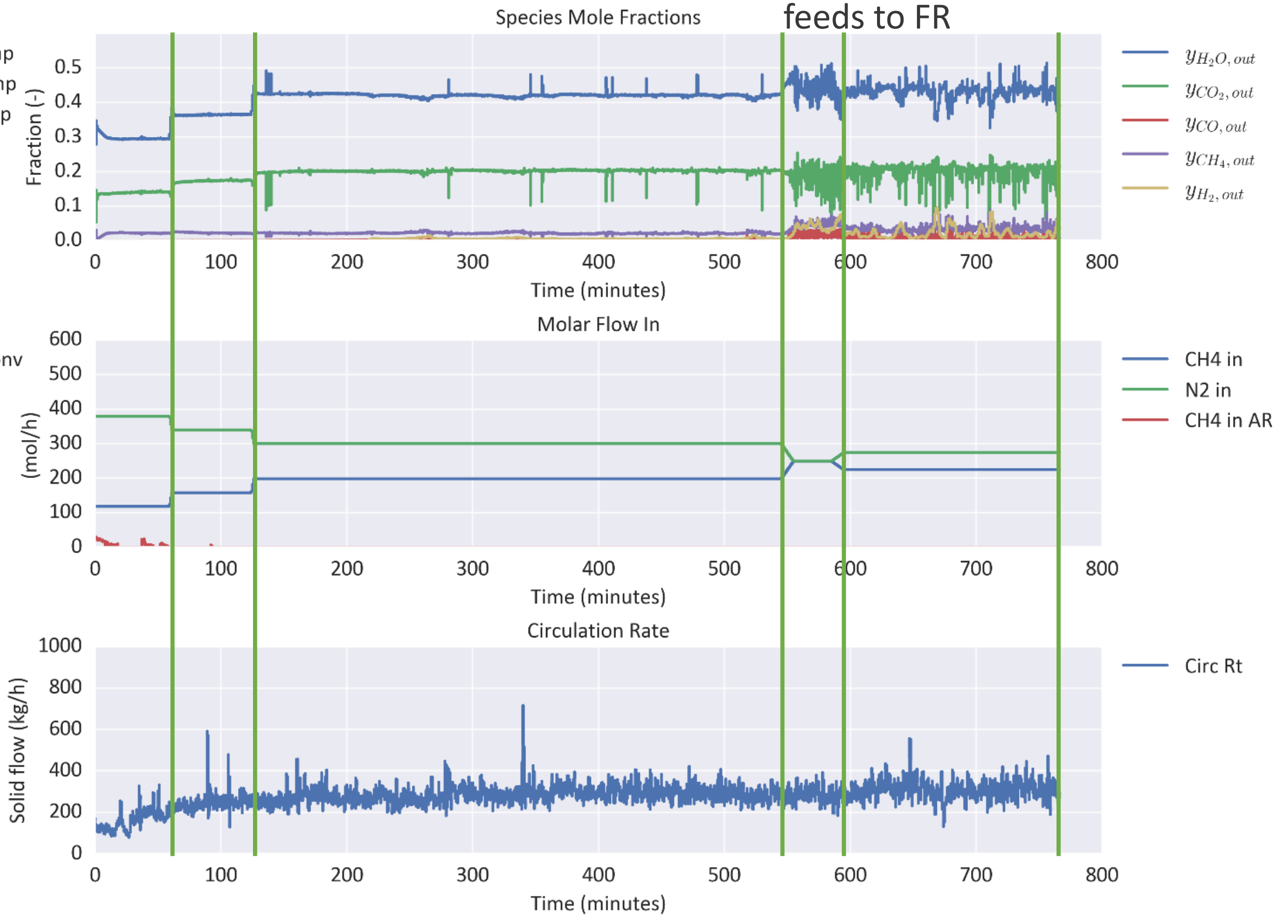
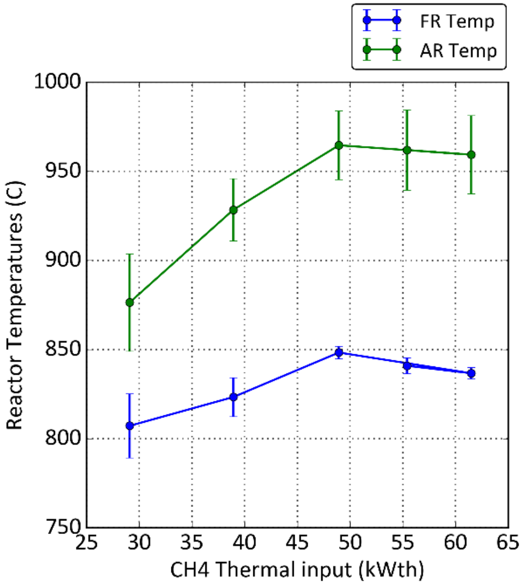
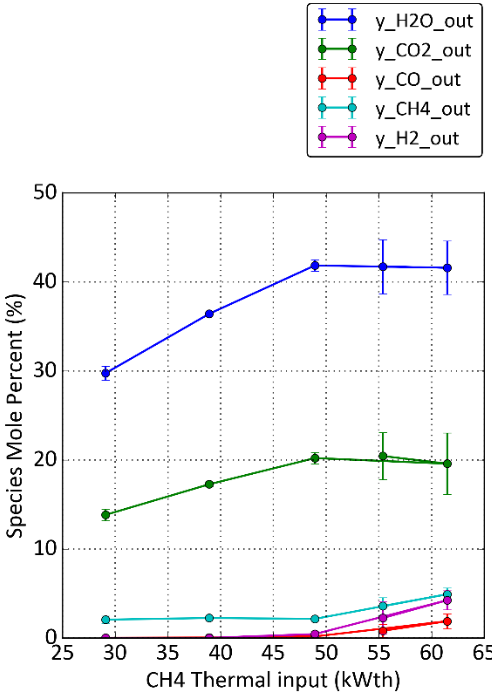


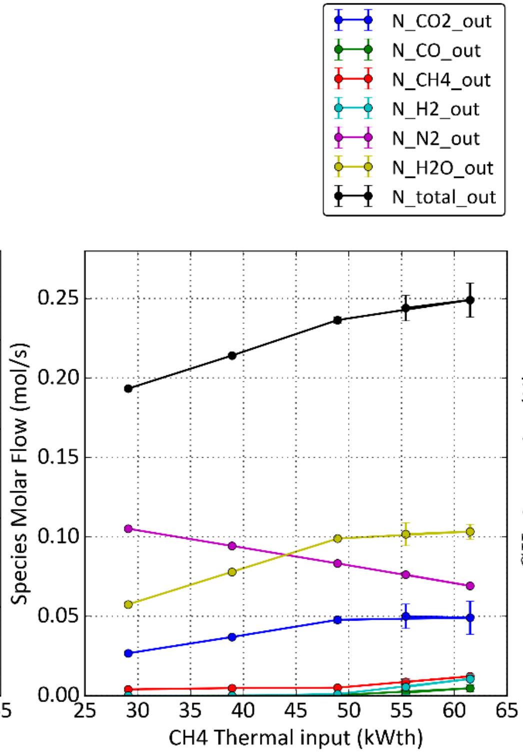
Autothermal trials

Plotted as a function of FR natural gas input

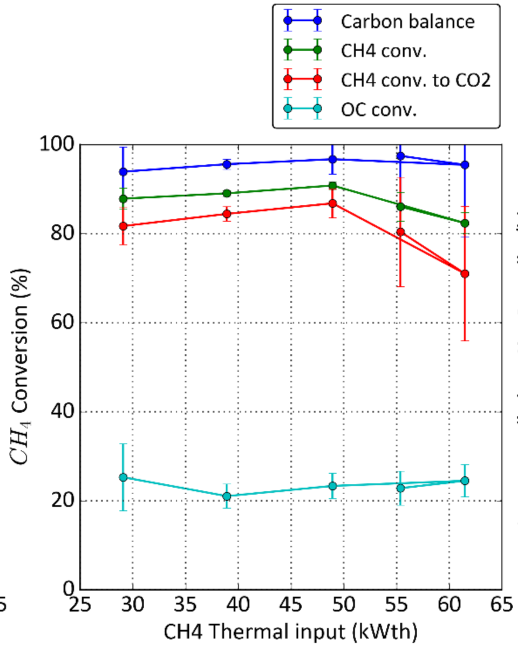


Temperature increased as more natural gas was fed into the FR

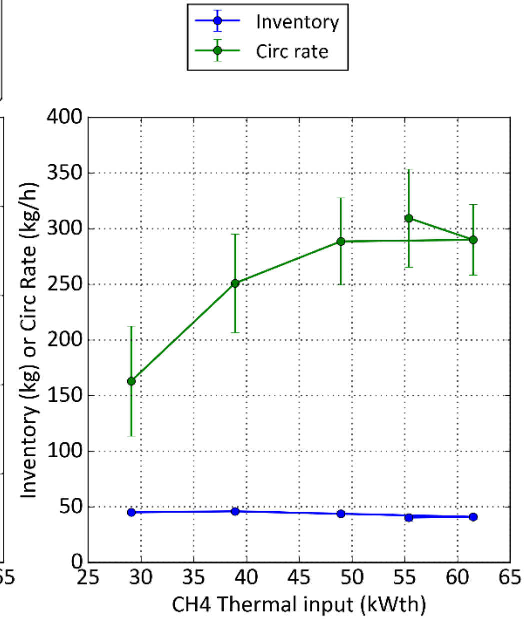




CO/H2 breakthrough occurred around 50 kWth



CH4 conversion performance increased as temperature increased but dropped above 50 kWth



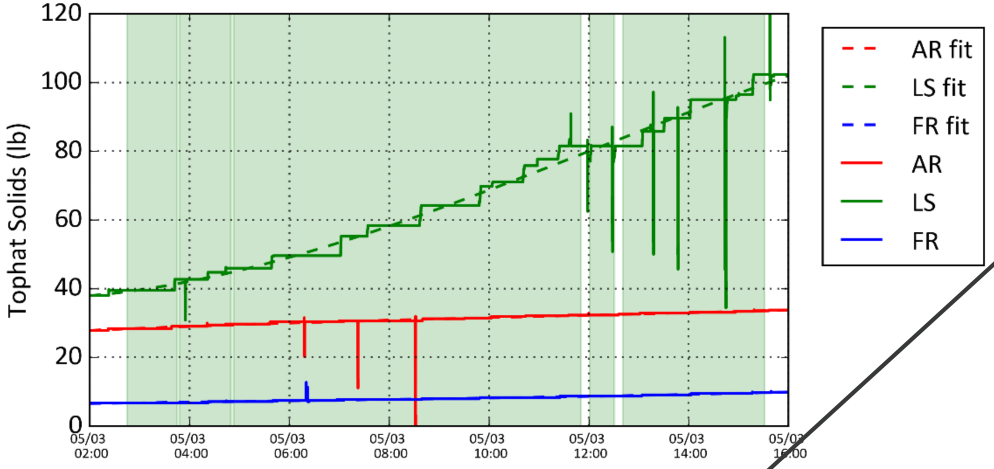
Circulation rate increased with higher natural gas concentration

- CH4 → 3 moles of gas products!

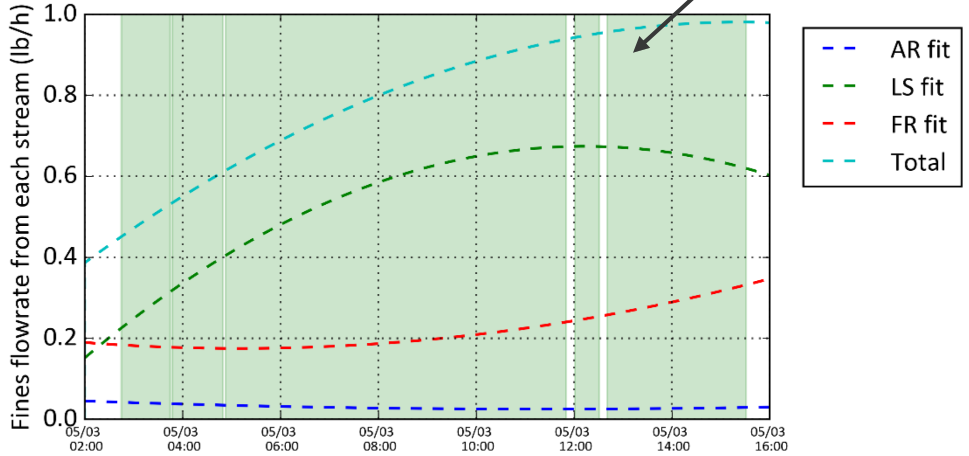
Determination of Attrition Rate

Calculated during Autothermal Trials (May 2017)

Collected solids from secondary cyclones



Derivative of curve fit of collected solids



Datafit of solids collection from secondary cyclones to a polynomial

$$\dot{m}_{attr} = \dot{m}_{FR} f^{m}_{FR,fines} + \dot{m}_{AR} f^{m}_{AR,fines} + \dot{m}_{LS} f^{m}_{LS,fines}$$

$\dot{m}_i$ = Rate of solids collected from secondary cyclones

$f^{m}_{i,fines}$ = Assumed mass fraction of fines in tophat

Fuel Reactor	92.4%
Loop Seal	11.8%
Cyclone	7.1%

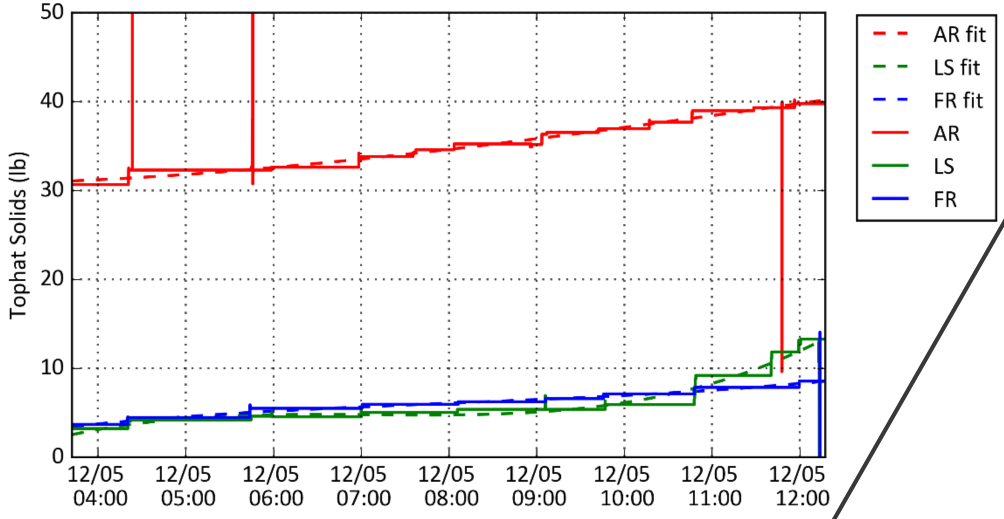
Fines defined as particles less than 150 micron

Limitations to analysis:

- Mass fraction of fines in each stream is assumed constant ("bulk value" measured at end of run)
- Does not take into account mass of fines collected in filter
- Derivative of polynomial fit is quite crude and does not capture subtlety of mass flows

Solids flows

Collected solids from secondary cyclones



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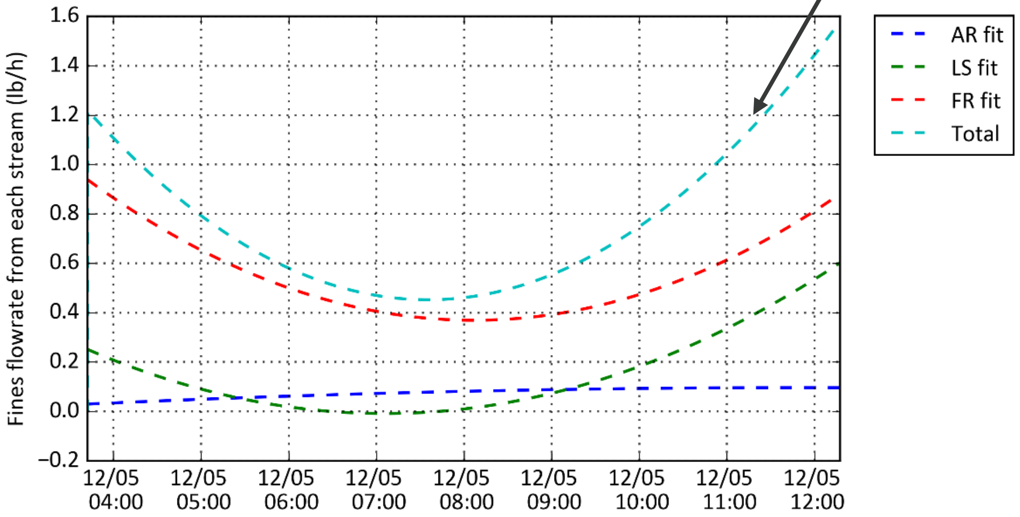
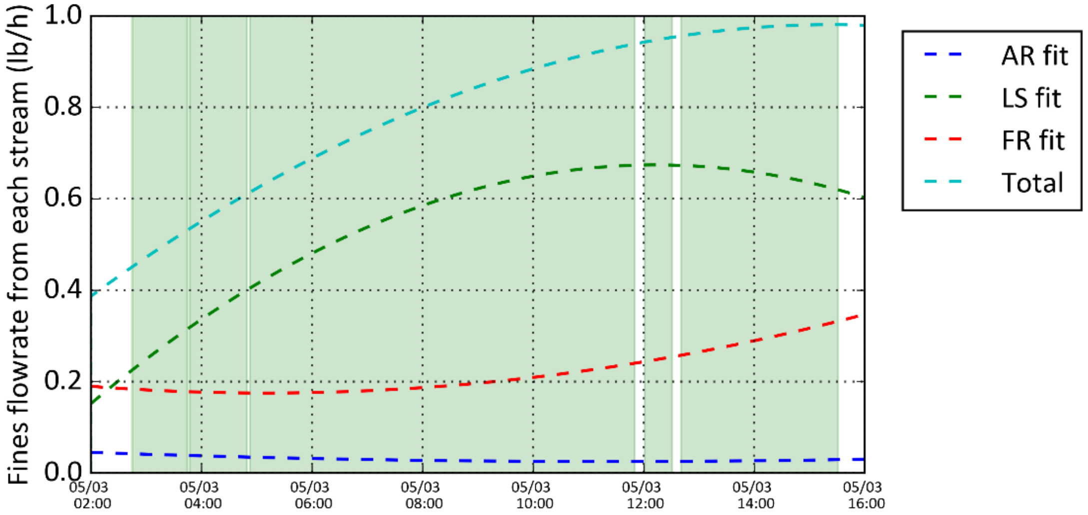


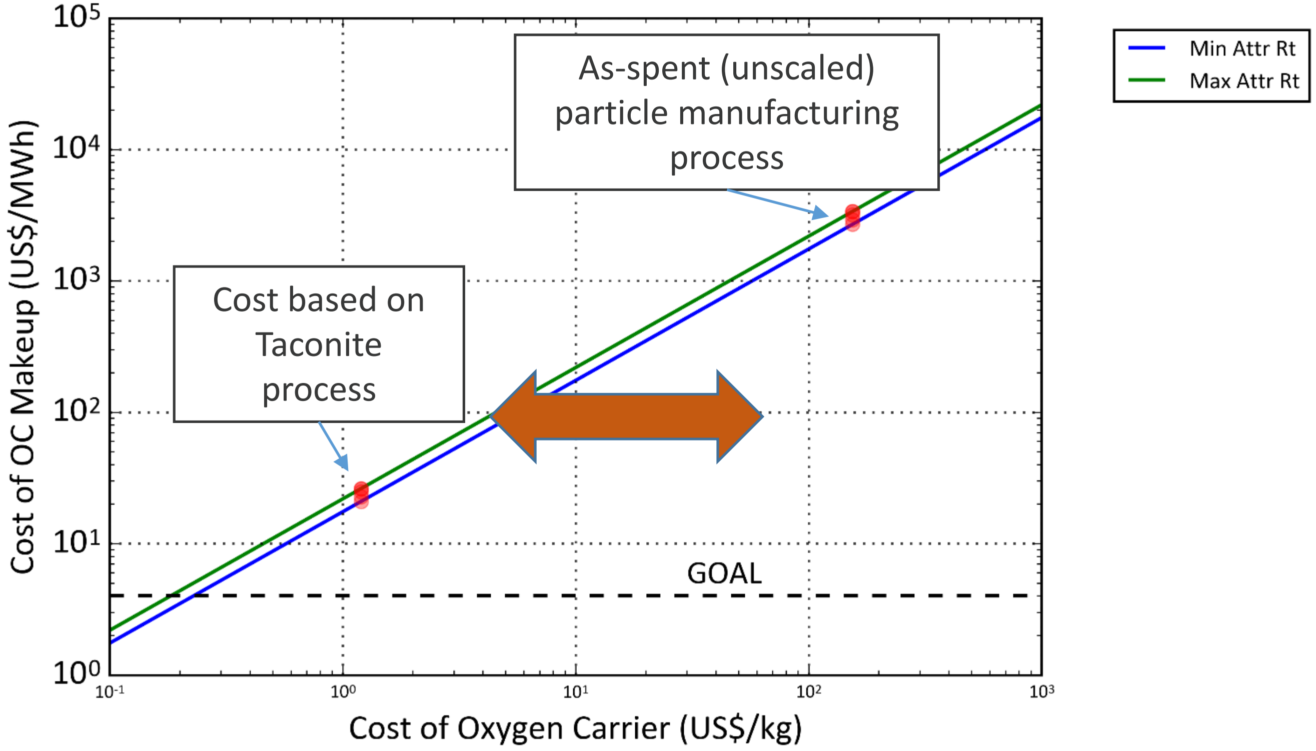
Similar order of magnitude of attrition rate from May 2017 run



NETL 50 kW_{th} Circulating CLC Testing

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

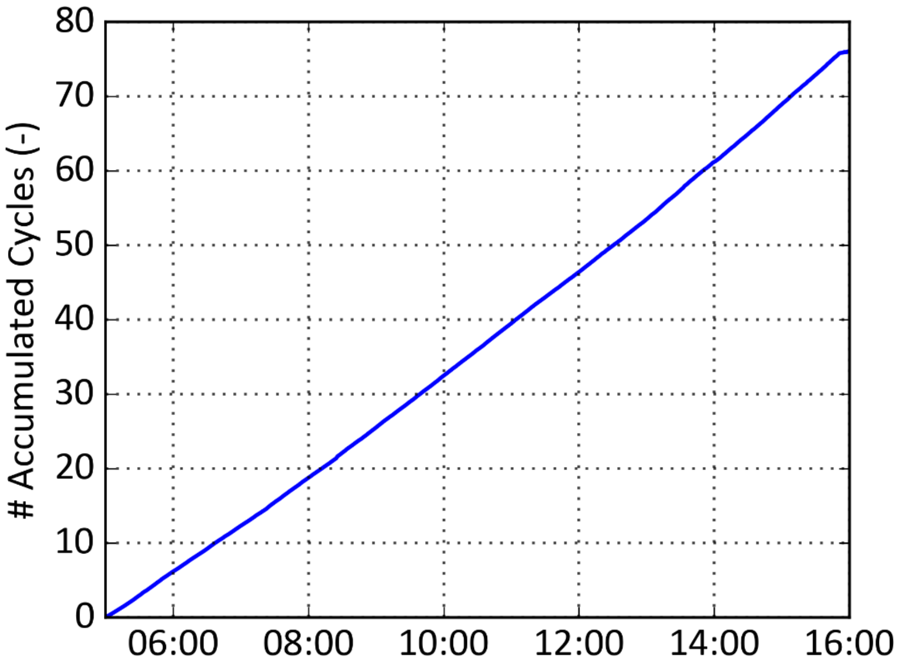
- O_2 carrier make-up costs
  - Baseline for 50kW_{th} test unit estimated
  - Key issue for CLC technology maturation
- Gaps to address . . .
  - Lower-cost O_2 carriers
  - Fundamental effects of redox cycling on attrition
  - Need longer duration tests under redox and circulating conditions
- More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



$$\text{Makeup Cost}\left(\frac{\$}{\text{MW}_{\text{th}}-\text{hr}}\right)=\frac{W_{OC}\dot{m}_{loss}(1-\alpha)}{\dot{N}_{CH_4,in}X_{CH_4\rightarrow CO_2}HHV_{CH_4}}\times\left(3.6\times10^6\frac{\text{kJ}}{\text{MWh}}\right)$$

Conclusions and Future Run Objectives

- 11 hours of autothermal with CuFe material performed with recycled solids
  - Methane conversion to CO2 ranged from 70-90%
  - Carrier underwent 75 oxidation-reduction cycles during autothermal trials (most of it at least)
  - Methane conversion increased up to a certain point (48 kWth), then decreased
  - Carbon and solid balances reasonable
  - Results repeatable from run in December 2017



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  - Rich Dennis, Dan Driscoll, John Rockey, Steve Markovich, Briggs White, Geo Richards
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