5-25-2016

Operating experience of a 50kwth methane chemical looping reactor

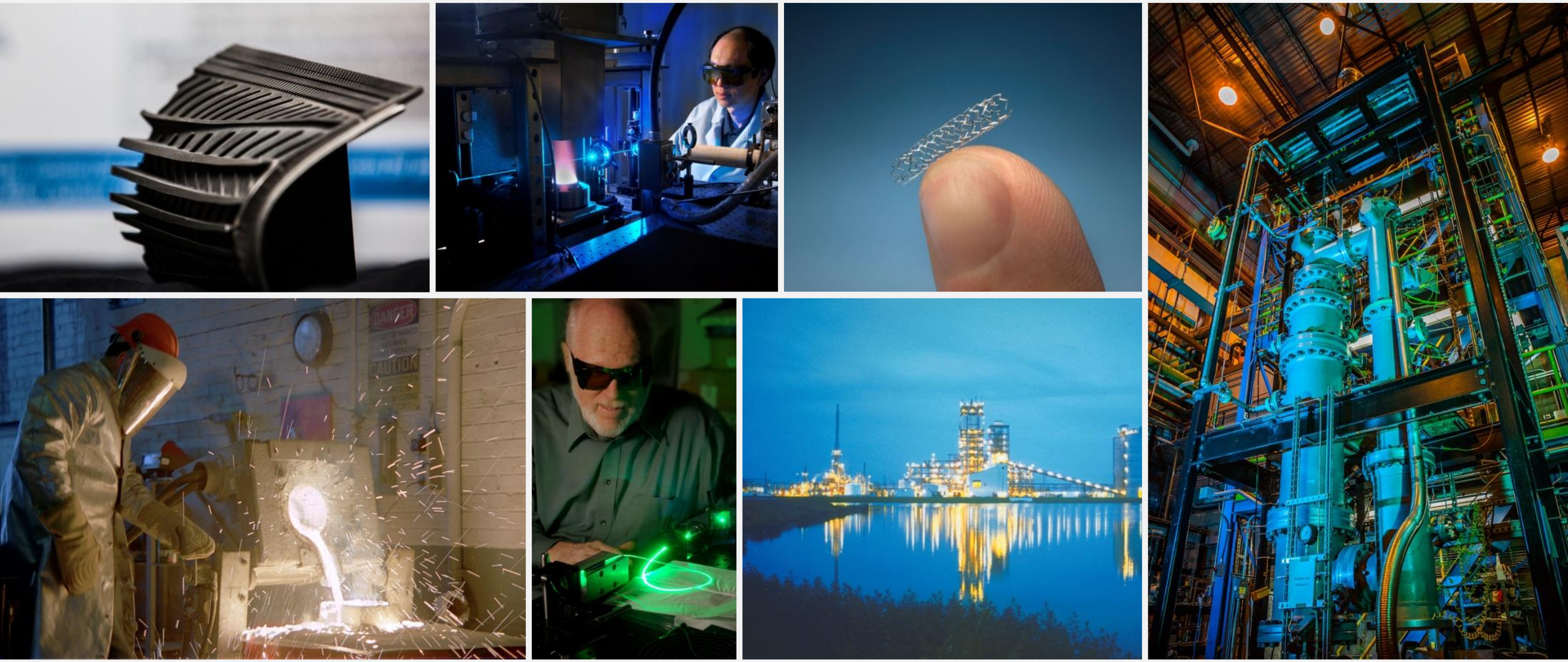
Ronald W. Breault
US Department of Energy's National Energy Technology Laboratory, ronald.breault@netl.doe.gov

Justin Weber
US Department of Energy's National Energy Technology Laboratory

Samuel Bayham
US Department of Energy's National Energy Technology Laboratory ; Oak Ridge Institute for Science and Education, 3610 Collins Ferry Road, Morgantown

Douglas Straub
US Department of Energy's National Energy Technology Laboratory

Driving Innovation ♦ Delivering Results



Justin Weber, Douglas Straub, Samuel Bayham, Ronald Breault
National Energy Technology Laboratory
US Department of Energy

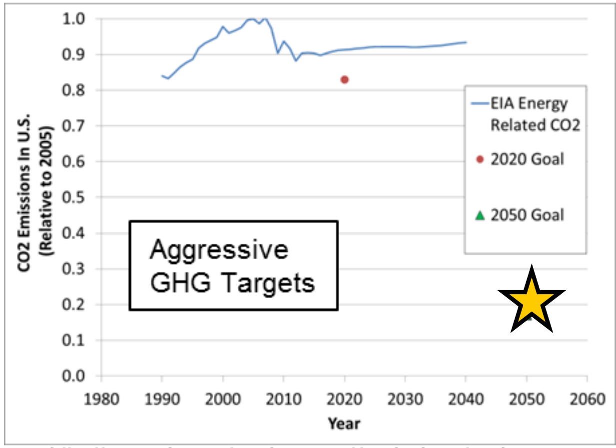
Operating Experience of a 50 kW_{th} Methane Chemical Looping Reactor

May 25, 2016

Motivation for this work

- **Presidential GHG reduction goals**
- **Domestic importance of fossil fuels**
  - Need fossil fuel options that produce minimal GHGs
- **CLC technology has "potential" to achieve DOE goals**

Presidential Energy-Related GHG Targets

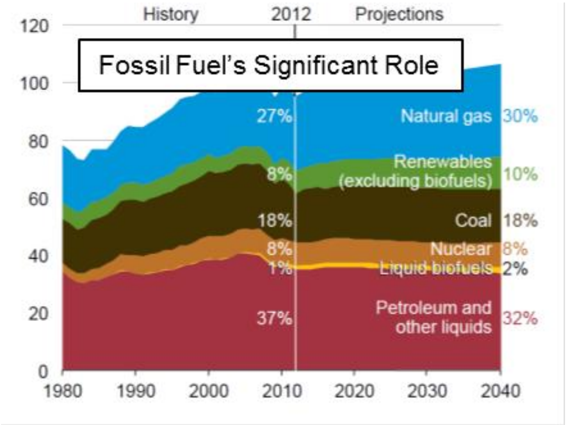


http://www.eia.gov/environment/emissions/carbon

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



AEO2014 – Early Release

Ref: U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL). Guidance for NETL's Oxycombustion R&D Program: Chemical Looping Combustion Reference Plant Designs and Sensitivity Studies. Pittsburgh : s.n., 2014. DOE/NETL-2014/1643

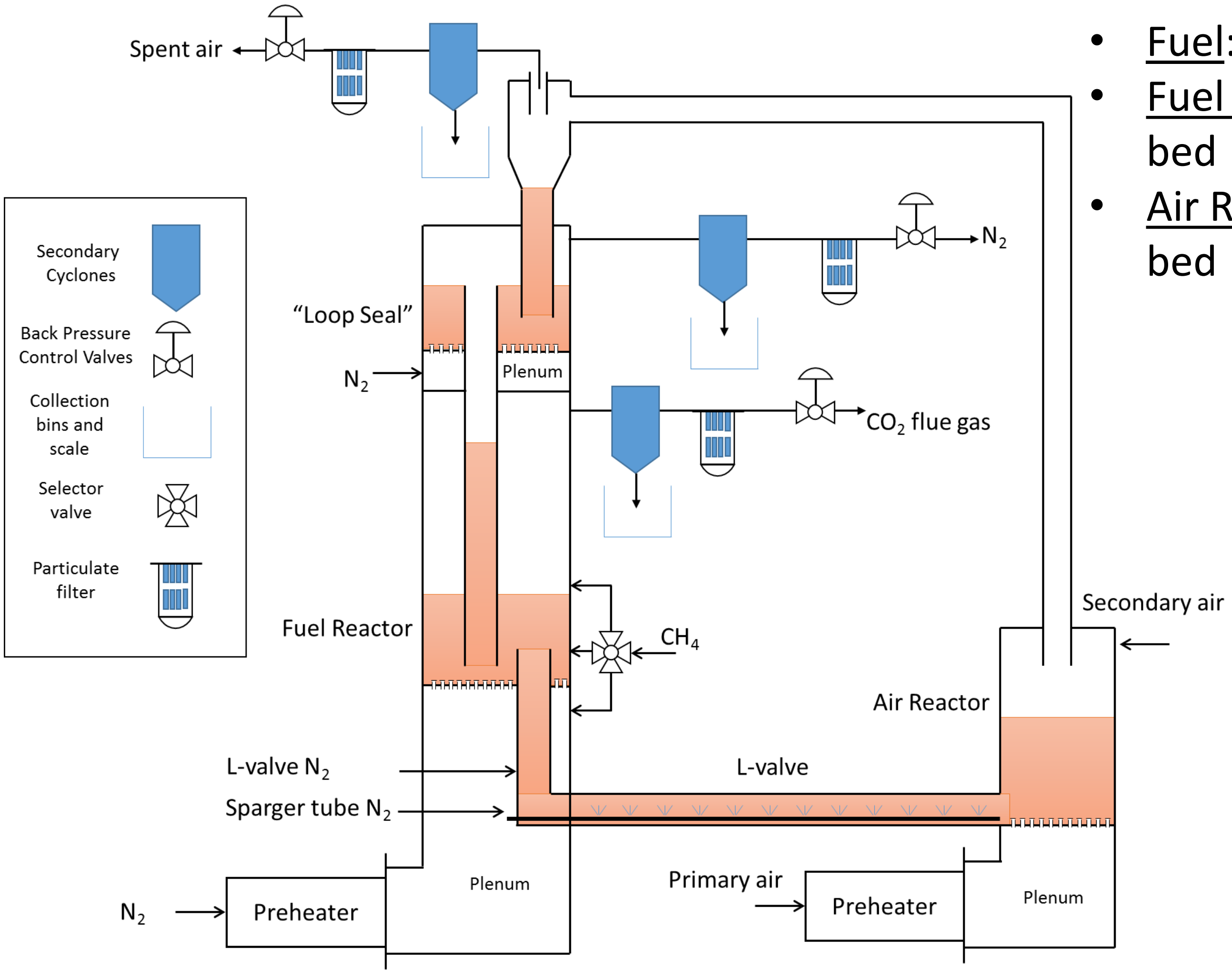
NETL's Chemical Looping Combustion

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
  - Ultimately commercialization

  → jobs and growth

Chemical Looping Reactor: Test Apparatus

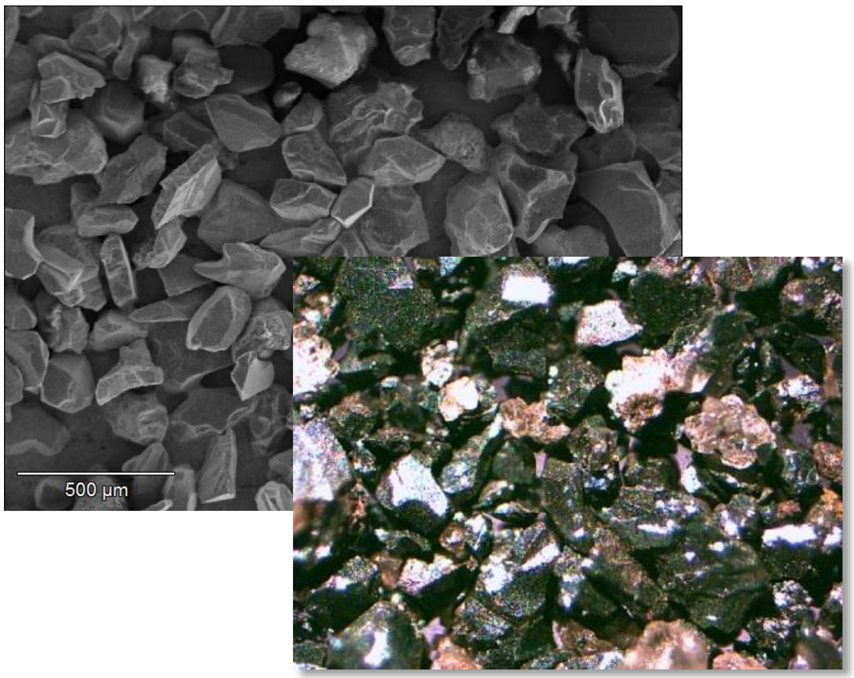


- Fuel: 50 kW_{th} Natural Gas
- Fuel Reactor: Bubbling fluidized bed
- Air Reactor: Bubbling fluidized bed

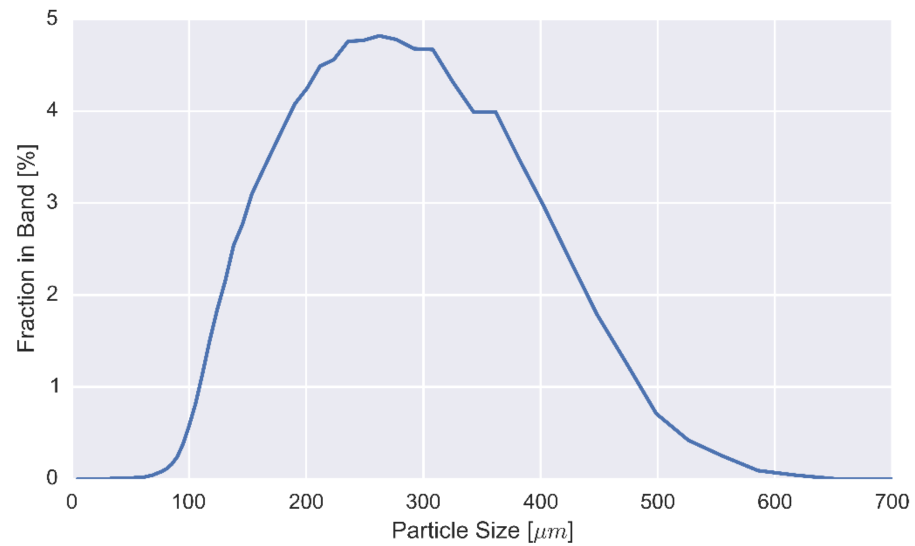
Oxygen Carrier Material: Raw Hematite

Hematite is a “baseline” oxygen carrier

Material: Natural Hematite Ore
Source: Wabush Mine, Canada



SEM and light microscopy of Hematite



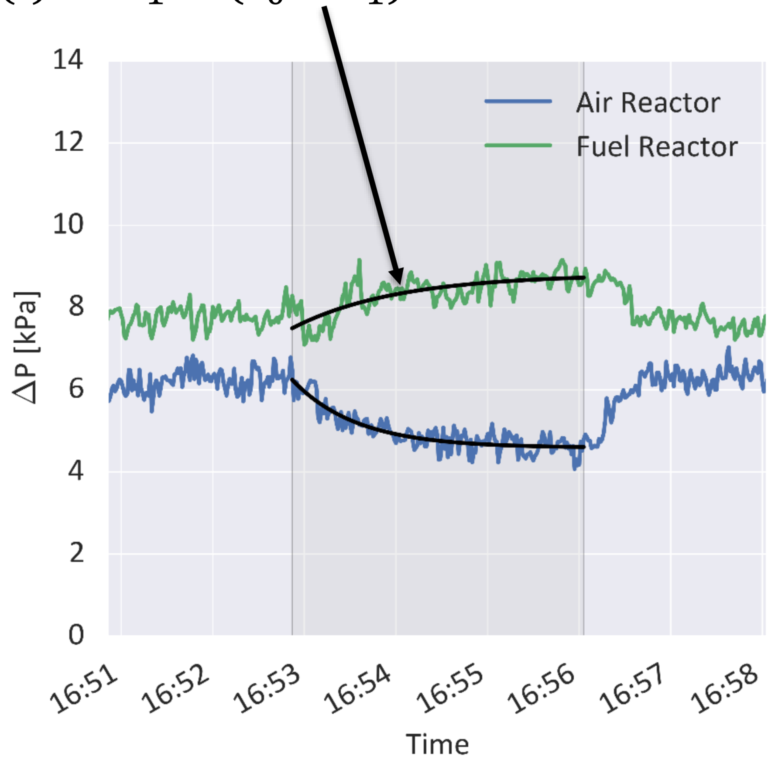
Particle density	4.9	g/cm^3
Sauter Mean Diam.	210	µm
D_{50}	238	µm
Sphericty	0.876	--
U_{mf} (at 298 K)	8.55	cm/s

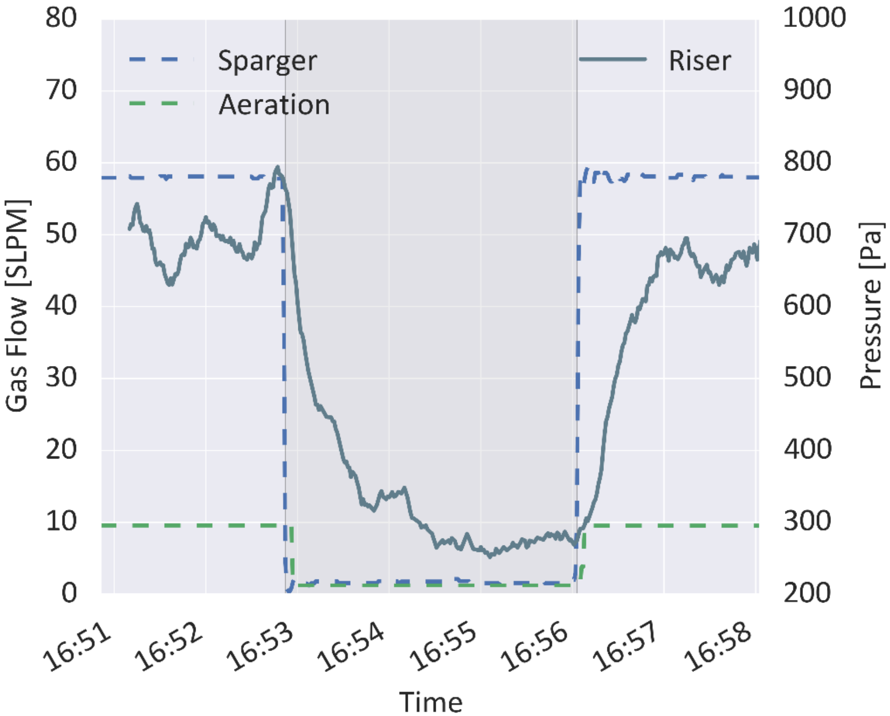
Determination of Solids Circulation Rate

$$\frac{dm}{dt} = \frac{A}{g} \cdot \frac{dP}{dt}$$

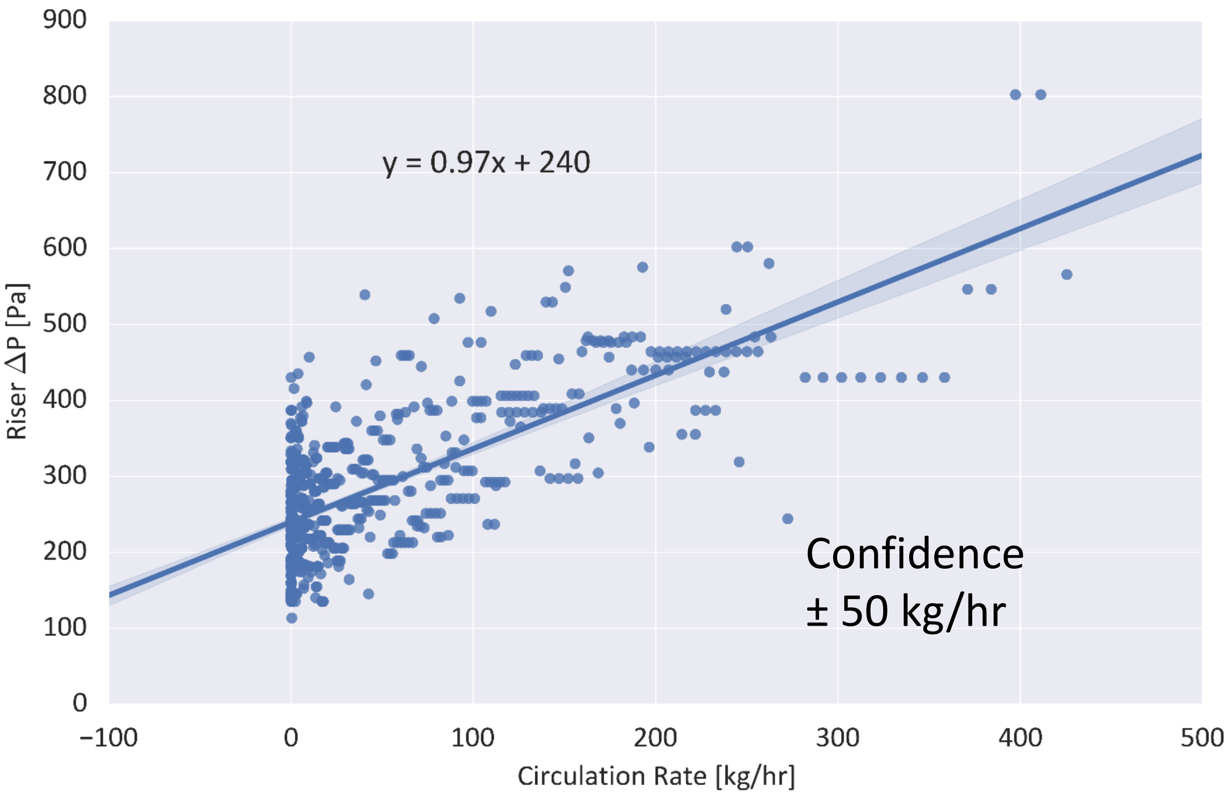
$$\Delta P(t) = P_1 + (P_0 - P_1)e^{-k(t-t_0)}$$

- L-valve cutoff tests were performed to measure the solids circulation rate
- Shutting off L-valve causes solids to build up in fuel reactor and exit the air reactor
- The pressure drop in the air and fuel reactors can be fit to an exponential to determine solids flow rate





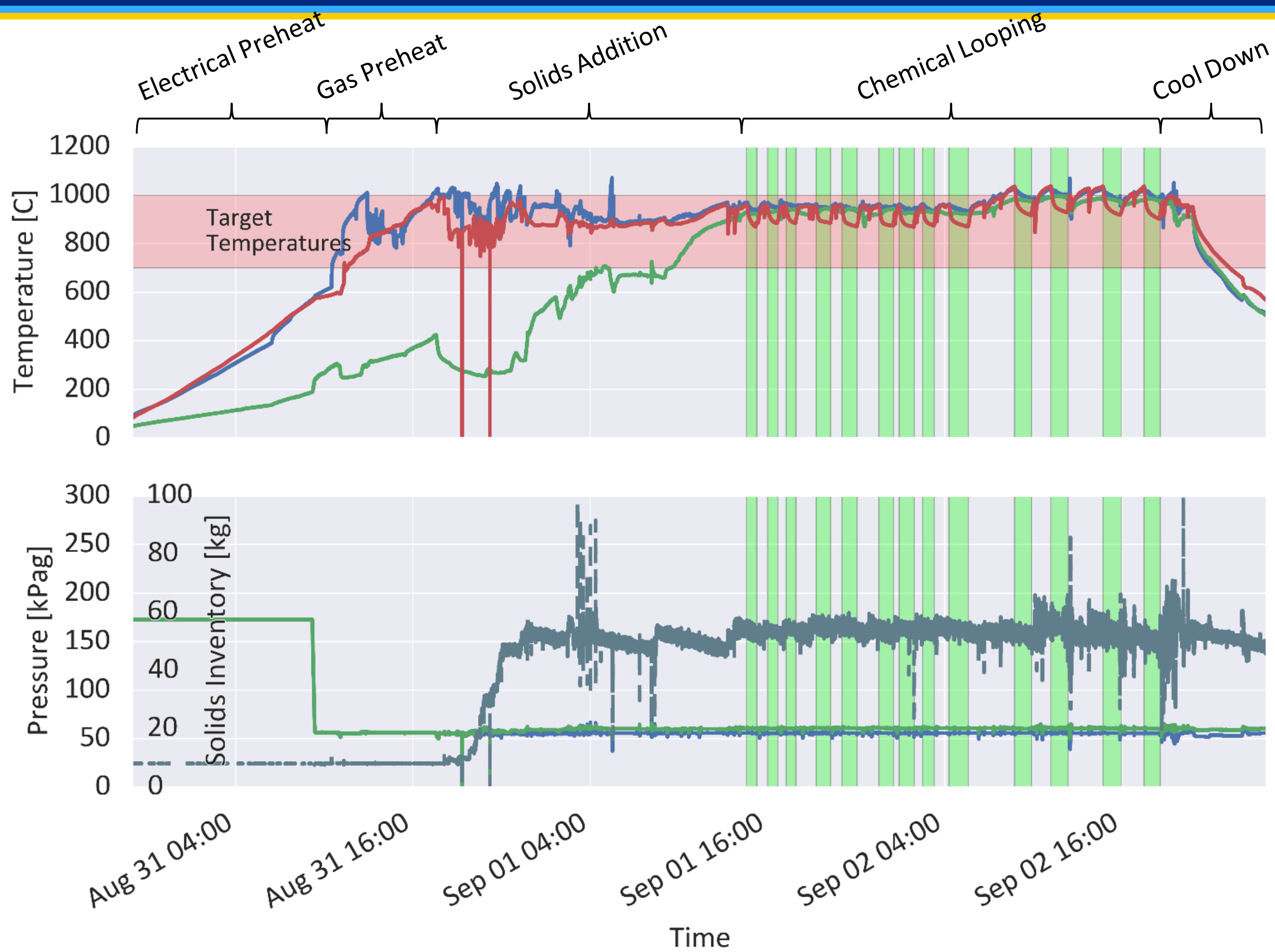
Circulation Rate Estimation Correlation



- Correlation created from riser pressure drop data and the calculated circulation rate from the L-valve cutoff tests
- Used for finding solids flow rate during trials based on riser pressure drop
- Standard error of data results in confidence of +/- 50 kg/hr
- Compares well with relation based on solids holdup

$$\dot{m}_s = \frac{(U_g - U_{term})A_{riser}}{g h_{riser}} \Delta P$$

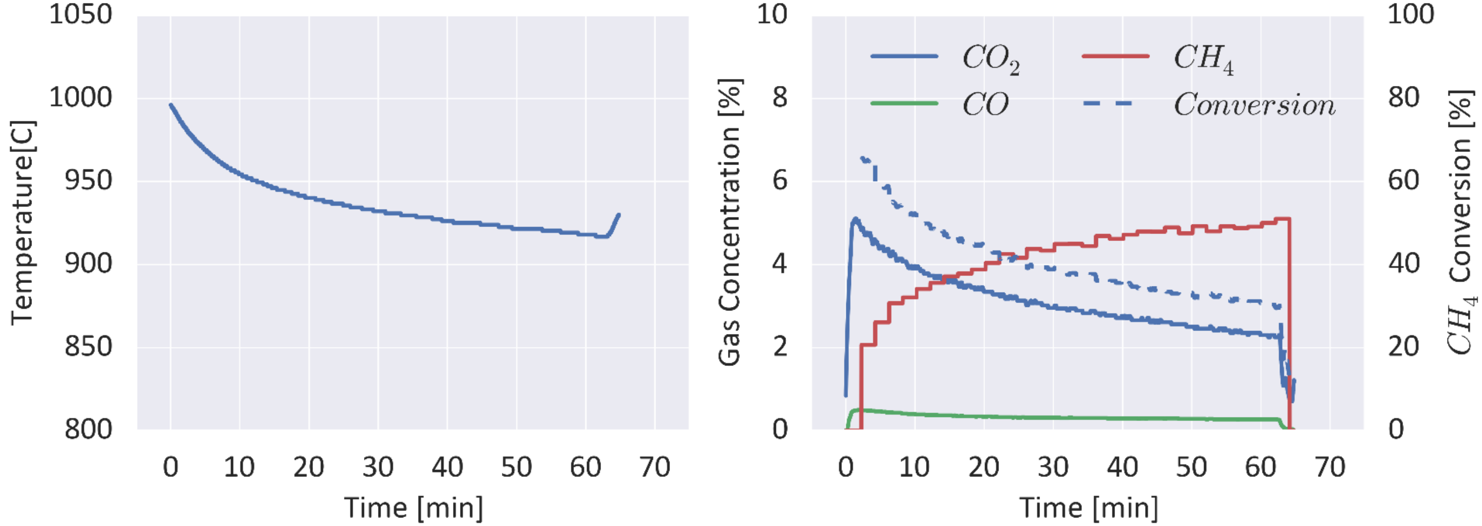
Chemical Looping Test Campaign



Test Duration: 3 days, 4 hours and 48 minutes

- **Electric preheat**
  - Room temperature → Auto-ignition temperature
- **Natural gas augmented preheat**
  - 1200F to 2000F
  - 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

Typical Chemical Looping Period



- Chemical looping tests began by transitioning from combustion mode in the fuel reactor (replacing air with nitrogen)
- Temperature in Fuel Reactor decays rapidly due to significant heat losses from the system and the endothermic reactions between CH_4 and hematite.
- Outlet gas concentration of CH_4 increases and the concentration of CO_2 decreases, and the methane conversion decreases (see Figure 7)

Performance Parameters

- 12 chemical looping tests periods
- 12.8 hrs of chemical looping
- Circulation rates ranged from 387 to 434 kg/hr
- Carbon balance ranged from 89 – 99%
- Methane conversion between 9-41%

Test	1	2	3	4	5	6	7	8	9	10	11	12
Duration [min]	41	40	59	62	59	61	47	78	70	69	74	66
Average FR Temperature [C]	895	894	892	881	881	880	886	884	936	944	936	922
Gas residence Time [s]	1.55	1.57	0.81	0.81	0.77	1.58	0.79	1.58	1.47	1.59	0.75	0.71
Methane Inlet Concentration	7%	14%	7%	14%	14%	14%	7%	7%	7%	14%	7%	15%
Circulation Rate [kg/hr]	389	400	434	431	415	387	419	390	398	434	431	411
Carbon Balance	92%	97%	97%	95%	99%	91%	98%	91%	89%	97%	97%	99%
CH4 Conversion	35%	26%	18%	9%	11%	27%	18%	27%	41%	35%	24%	15%

Methane Conversion

$$X_{CH_4} = \frac{\chi_{CO_2,out}}{\chi_{CH_4,in}}$$

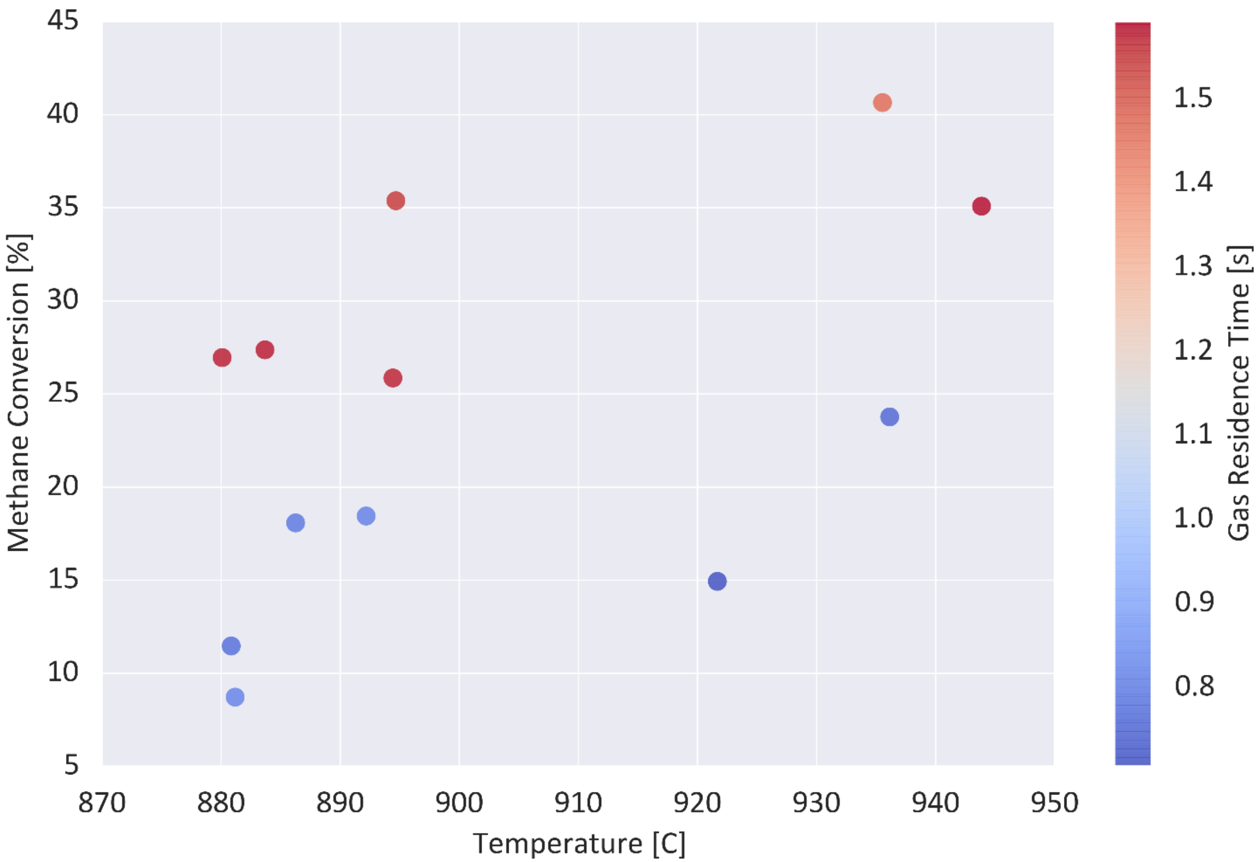
Carbon Balance

$$C_{\text{balance}} = \frac{\chi_{CO_2,out} + \chi_{CO,out} + \chi_{CH_4,out}}{\chi_{CH_4,in}}$$

Mean Gas Residence Time

$$\tau = \frac{h_{bed}}{V_{gas}} \quad , \quad h_{bed} = \frac{\Delta P}{\rho_s g (1-\varepsilon)}$$

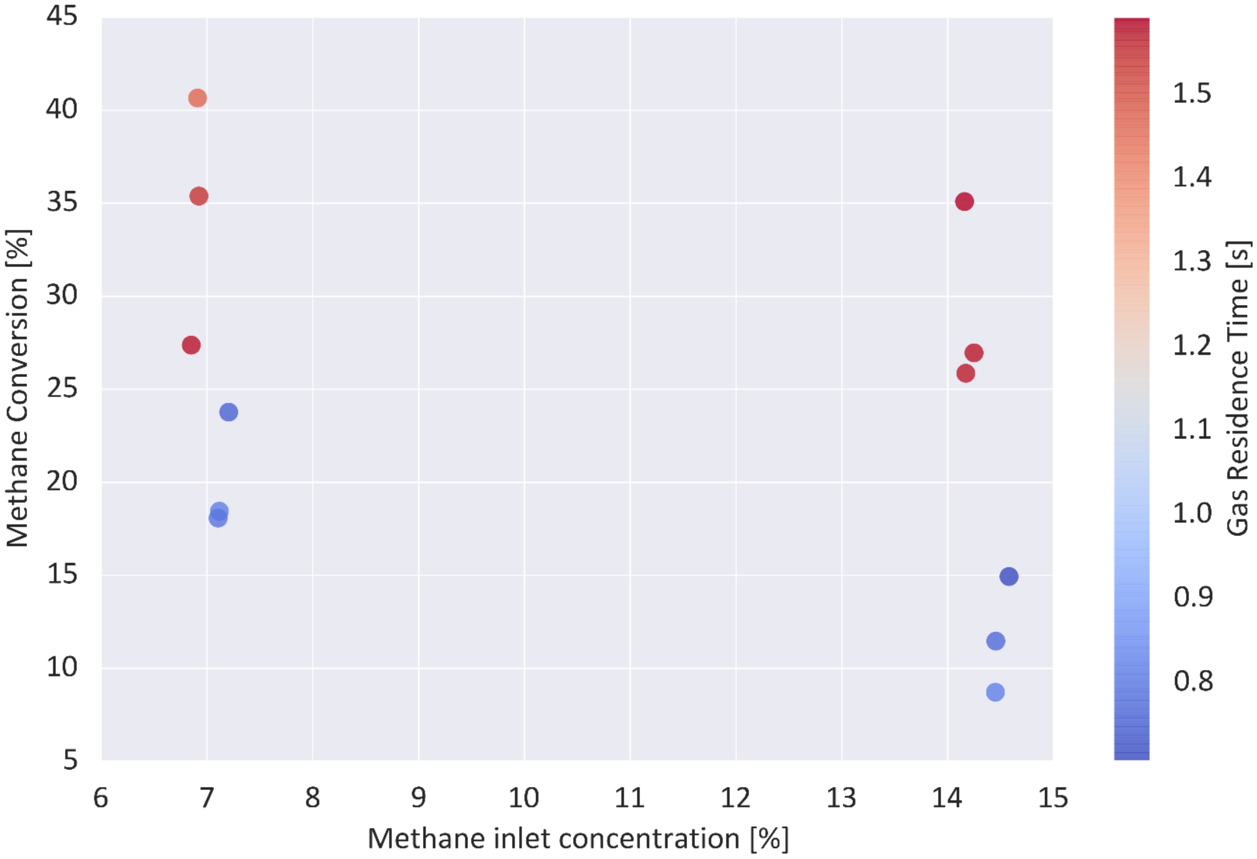
Effect of Fuel Reactor Temperature



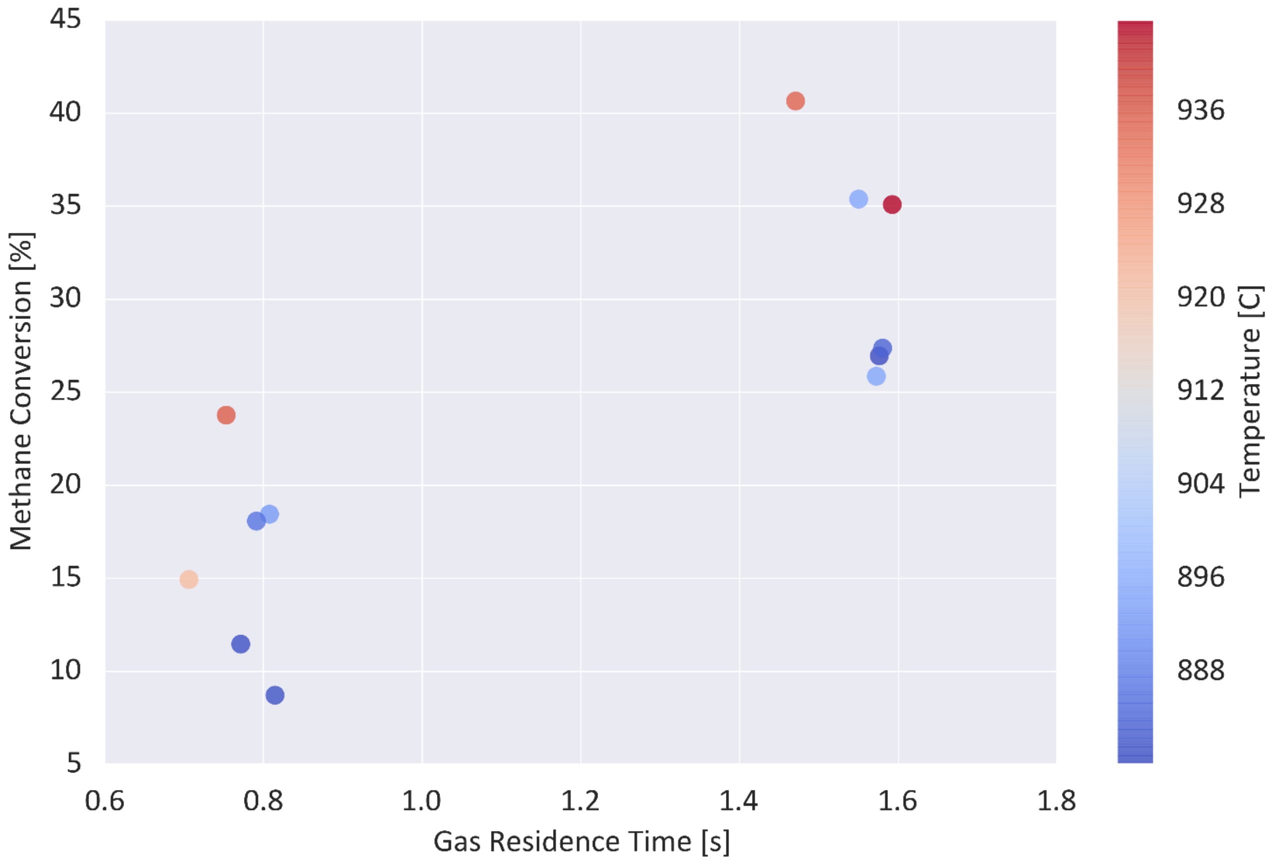
- Average temperature in fuel reactor has a strong effect on conversion
- Trials with similar gas residence times show increase in conversion with temperature
- Scatter due to variability in solids circulation rate

Effect of Inlet Methane Concentration

- For similar gas residence times, greater methane inlet concentrations result in lower methane conversions
- Scatter due to variance in solids circulation rate

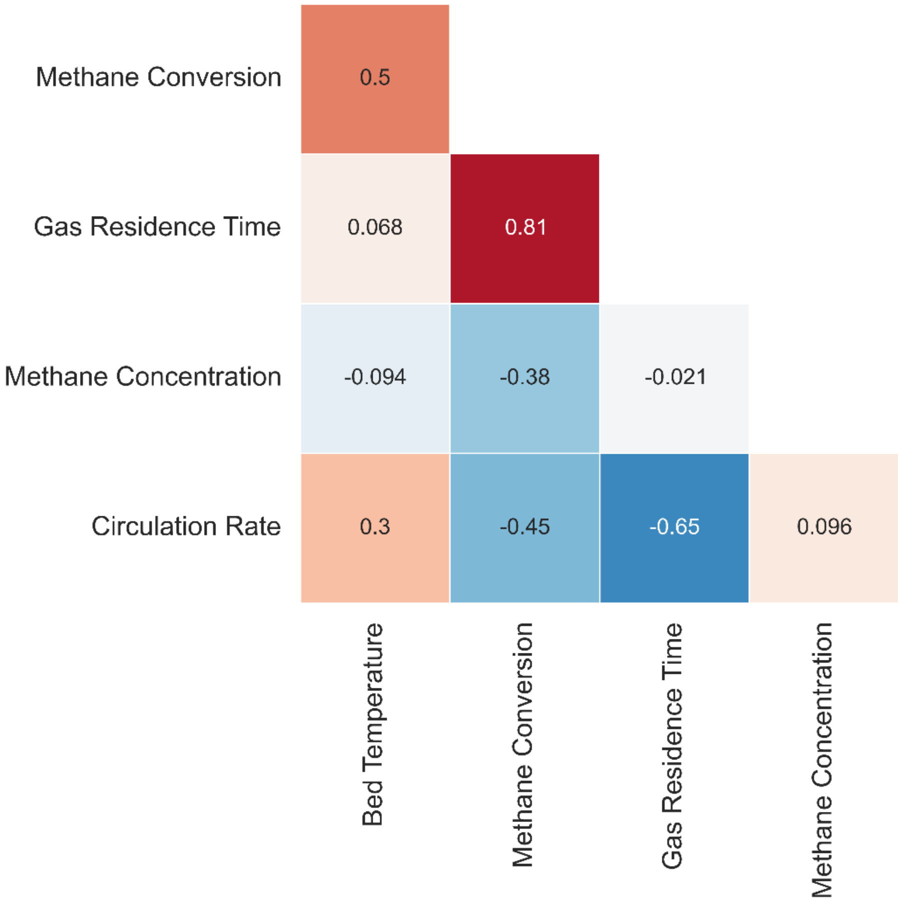


Gas Residence Time



- As the gas residence time increases, the methane conversion increases.
- The data is scattered because the temperature and solid circulation rates are changing between conditions.

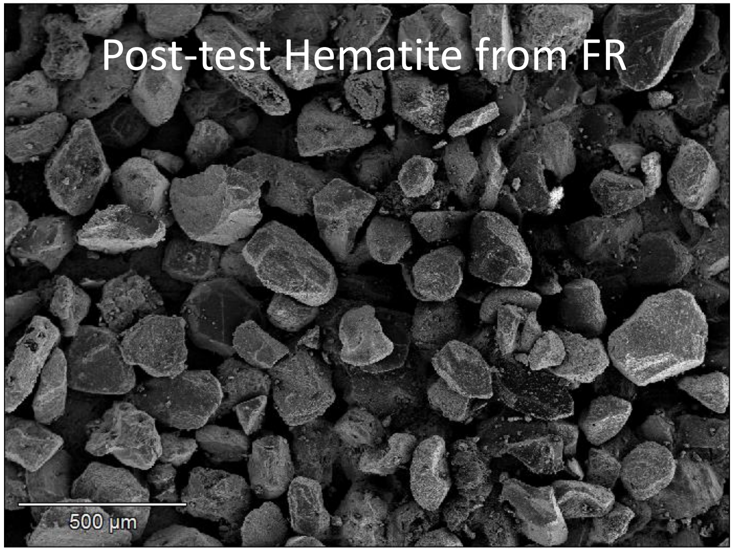
Pearson Correlation Matrix



- Pearson correlation coefficients were calculated for the various combination of experimental parameters
- Strongest relationship identified between gas residence time and methane conversion ($r_{pearson}$ =0.81)
- A strong relationship between the bed temperature and the methane conversion is identified($r_{pearson}$ =0.5)
- The inverse relationship between the inlet methane concentration and the methane conversion is also identified ($r_{pearson}$ = -0.38)

Post Test Analysis

- Carrier agglomeration in Fuel Reactor near bubble caps



Summary

- Chemical looping tests utilized a natural hematite ore that has a relatively low reactivity, conducted at temperatures that ranged from 850 – 1000°C.
- The oxygen carrier circulation rates for these tests were on the order of 400 kg/hr, and the conversion of methane to carbon dioxide ranged from 9-41%.
- The fuel reactor temperature and the bulk gas residence time through the fuel reactor bed are two factors that have a significant effect on the observed fuel conversion.
- The hematite oxygen carrier material seems to be a very durable mineral for chemical looping combustion applications, but the reactivity is very poor.
- There are also some indications that this material could experience some agglomeration issues if the operating temperature exceeds 1000°C.

Acknowledgements

- The authors would like to acknowledge the financial and technical support of DOE’s Advanced Combustion Program.
- Operating and support staff : Dave Reese, Jeffrey Riley, Mark Tucker, Richard Eddy, Stephen Carpenter, and the late James Spenik.
  - Without the contributions of these people, this work would not be possible!
- Research was also supported in part by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education.

Disclaimer

Thanks