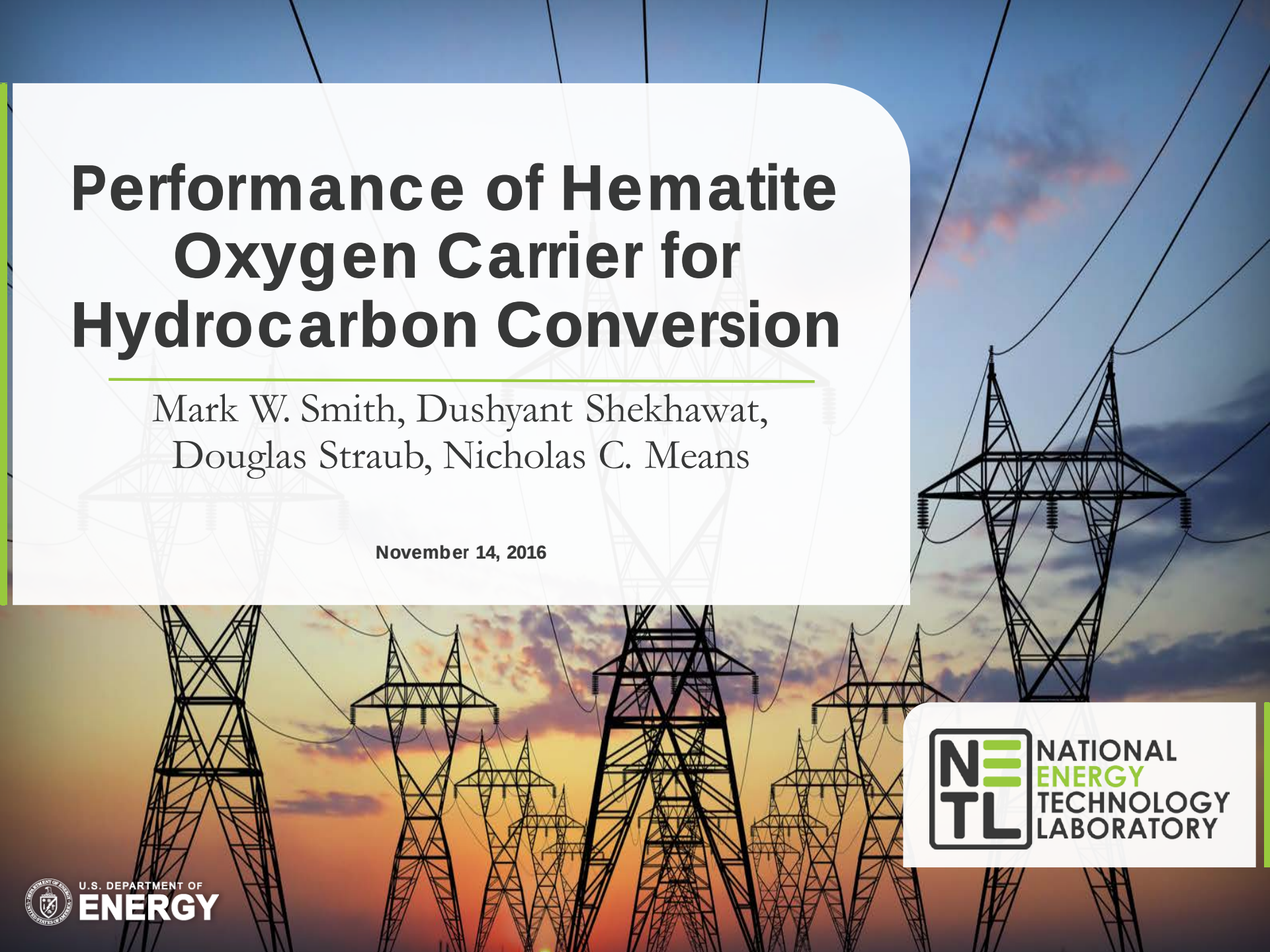
Performance of Hematite Oxygen Carrier for Hydrocarbon Conversion

Mark W. Smith, Dushyant Shekhawat,
Douglas Straub, Nicholas C. Means

November 14, 2016



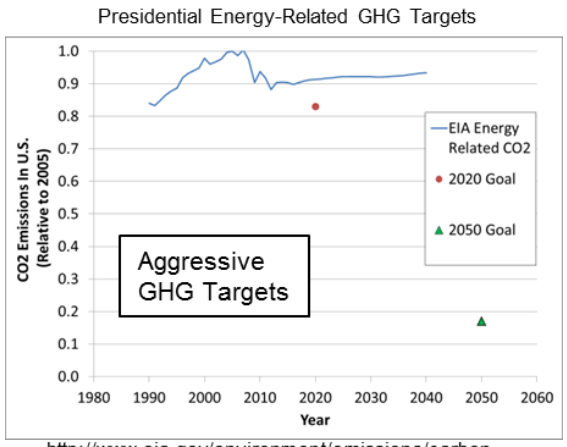
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

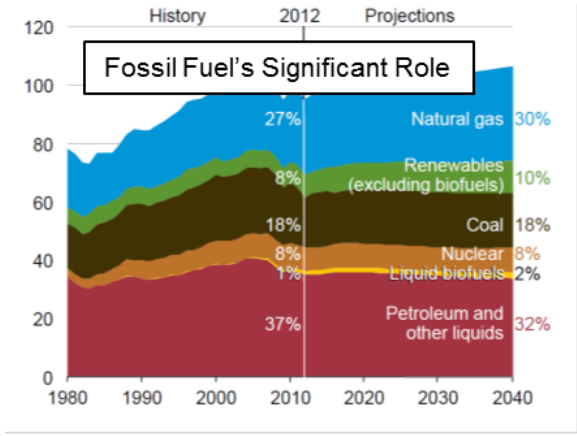
Background/Motivation

- GHG reduction goals are aggressive
  - EPA Clean Power Plan targets 30% reduction by 2030
  - 85% reduction by 2050
- Fossil fuels are important for domestic energy security and reliability
- Options to reduce GHGs for fossil fuels are needed
  - Post-combustion and pre-combustion CO_2 capture
  - Oxy-combustion
  - Chemical looping combustion
  - Pressure gain combustion
  - Direct-fired supercritical CO_2

Advanced Combustion



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



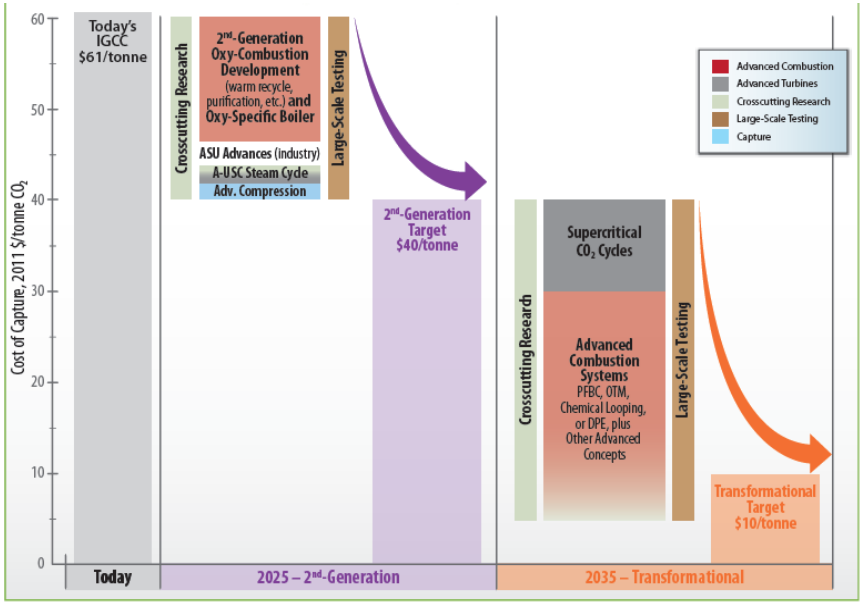
AEO2014 – Early Release

Adv. Combustion

Why Is NETL/RIC Doing This Work?

- Determine if options are technically feasible
  - Gather data and information for strategic decision making
    - → Is technology worthy of additional investment and development?
- If it is feasible, THEN
  - Help developers overcome technical issues
  - Help technology be successful
  - Ultimate commercialization → produces jobs and growth

Advanced Combustion NETL R&IC Focus



Advanced Combustion Systems Technology Program Plan, http://www.netl.doe.gov/research/coal/energy-systems/advanced-combustion,

Advanced Combustion: CLC

Where Are We Now?

- 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

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

Objectives

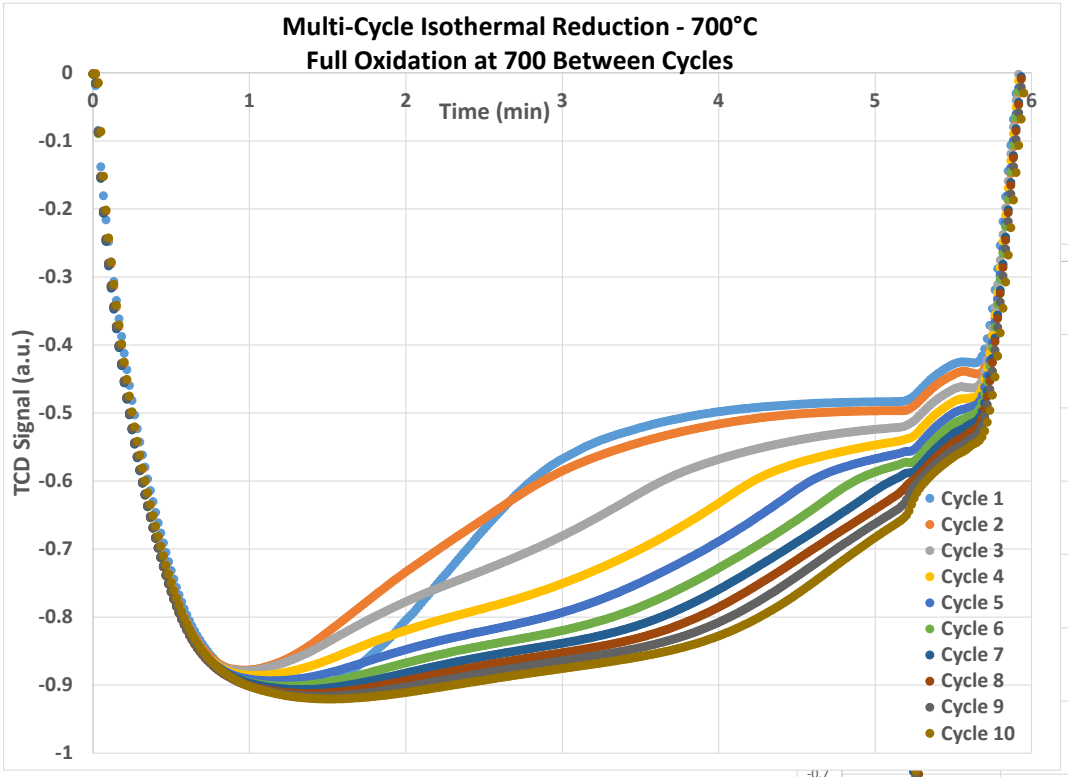
- Produce a data set to develop a kinetic model for incorporation into a CFD model; used to design and optimize complete CLC system
- Examine effect of several reaction parameters on oxygen carrier (OC) performance to determine most significant
- Observe how performance of OC changes over time and property changes that may account for them
- Identify and propose additional experiments for completing kinetic model

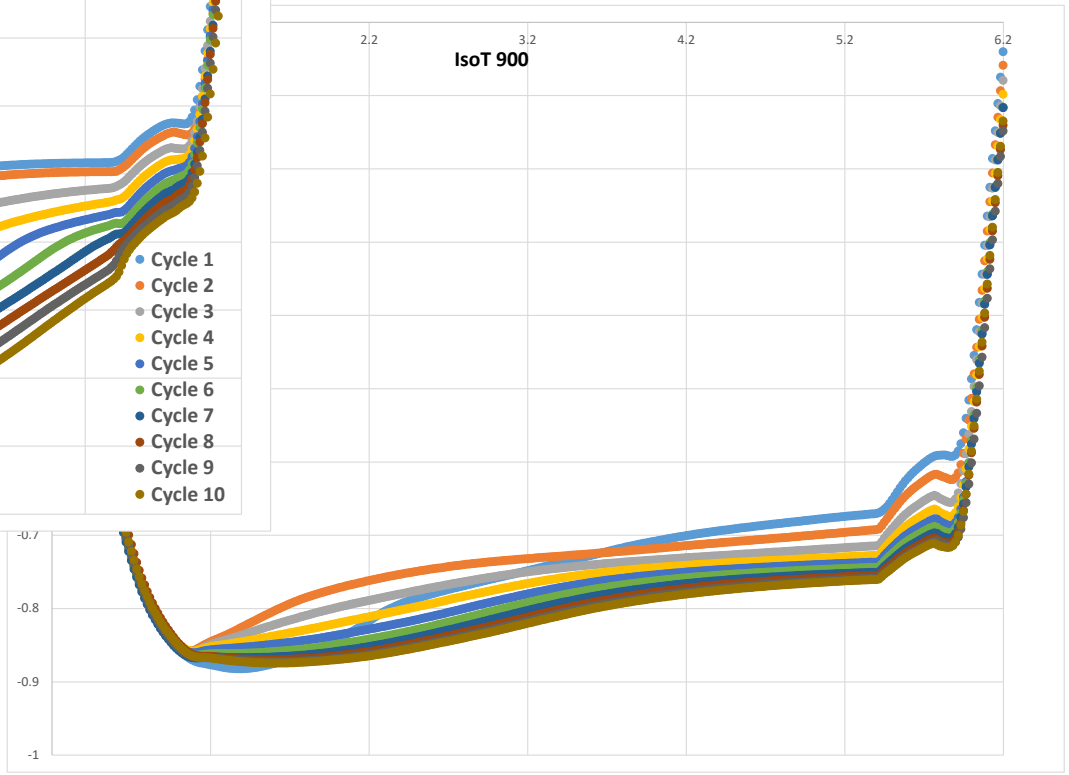
Experimental

- Multicycle Isothermal Reaction/Oxidation (Micromeritics 2950HP)
  - 10% H_2 (Ar bal.) / Air
  - 10% CH_4 (Ar bal.) / Air
- Operating Conditions
  - Mass Canadian Hematite = 0.2 g
  - Gas flow rate = 30 sccm
  - T = 700, 800, 900°C
  - Cycle time = 5 min
  - 10 cycles per run
- SEM/EDS – Fresh and Spent (900°C)

Hematite Reduction/Oxidation

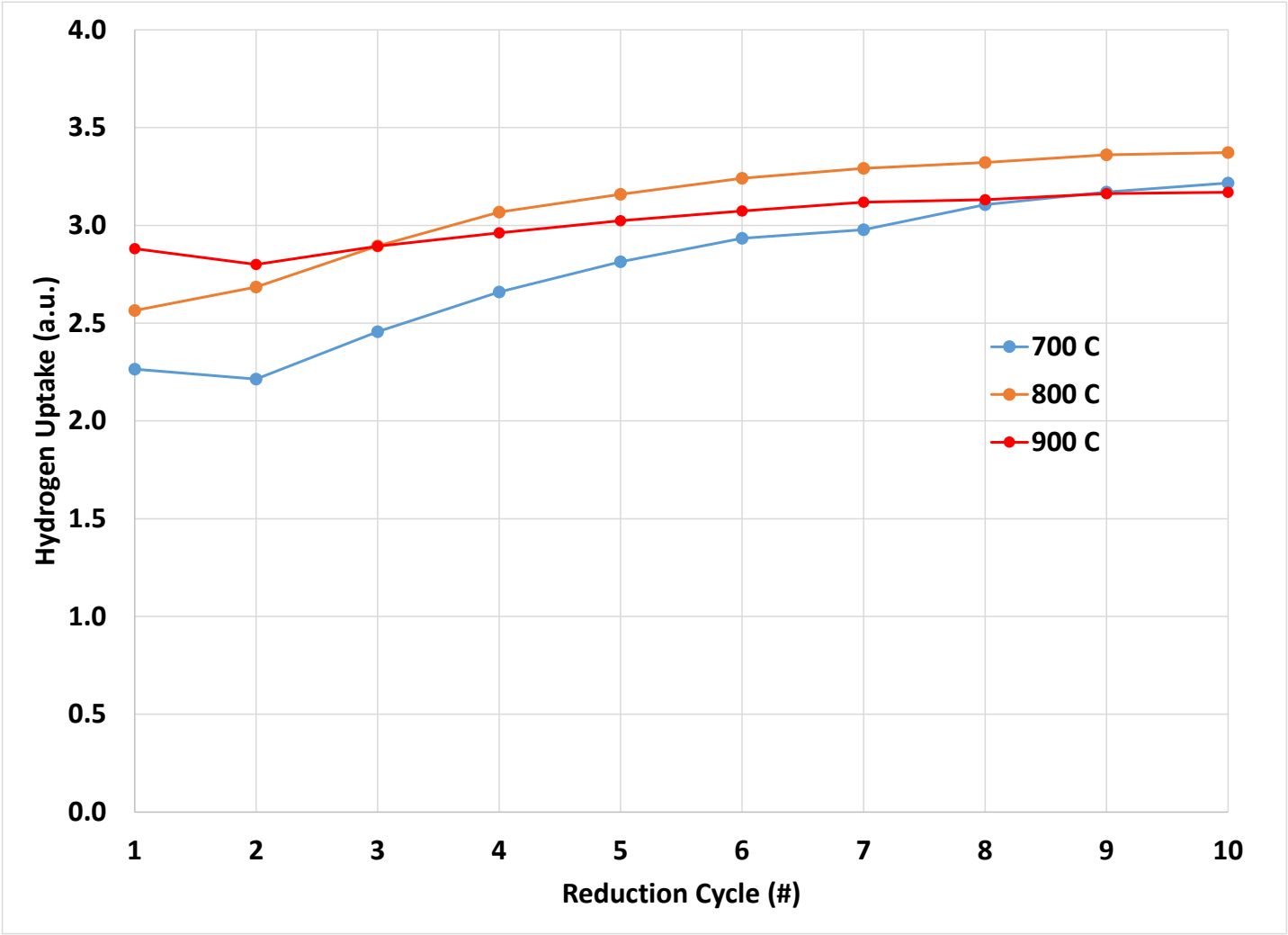
Multicycle Hydrogen Reduction/Air Oxidation





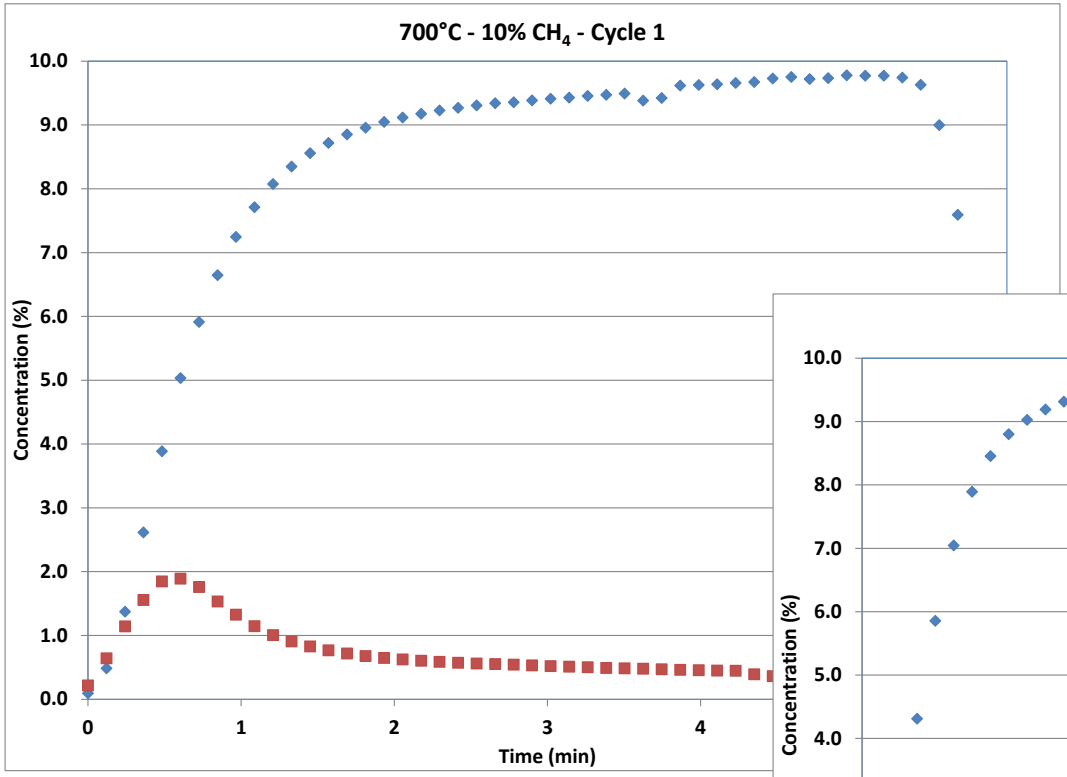
Hematite Reduction/Oxidation

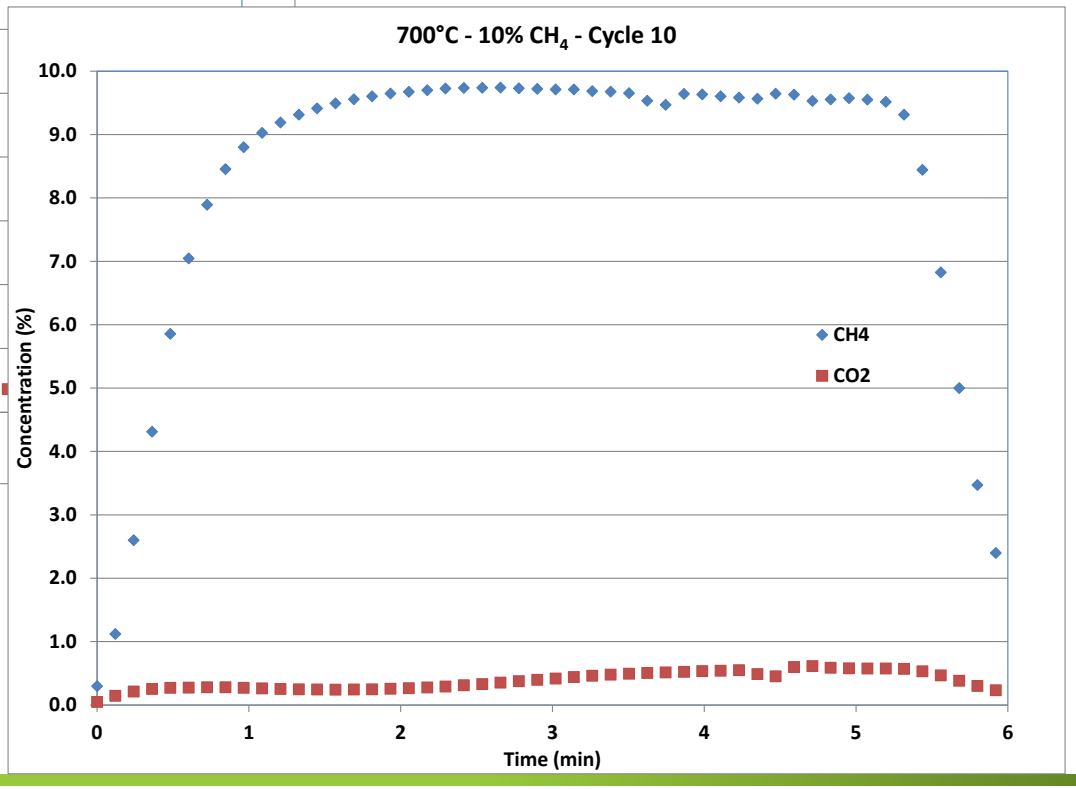
Effect of Temperature



Hematite Reaction

Multicycle CH4/Air Experiments





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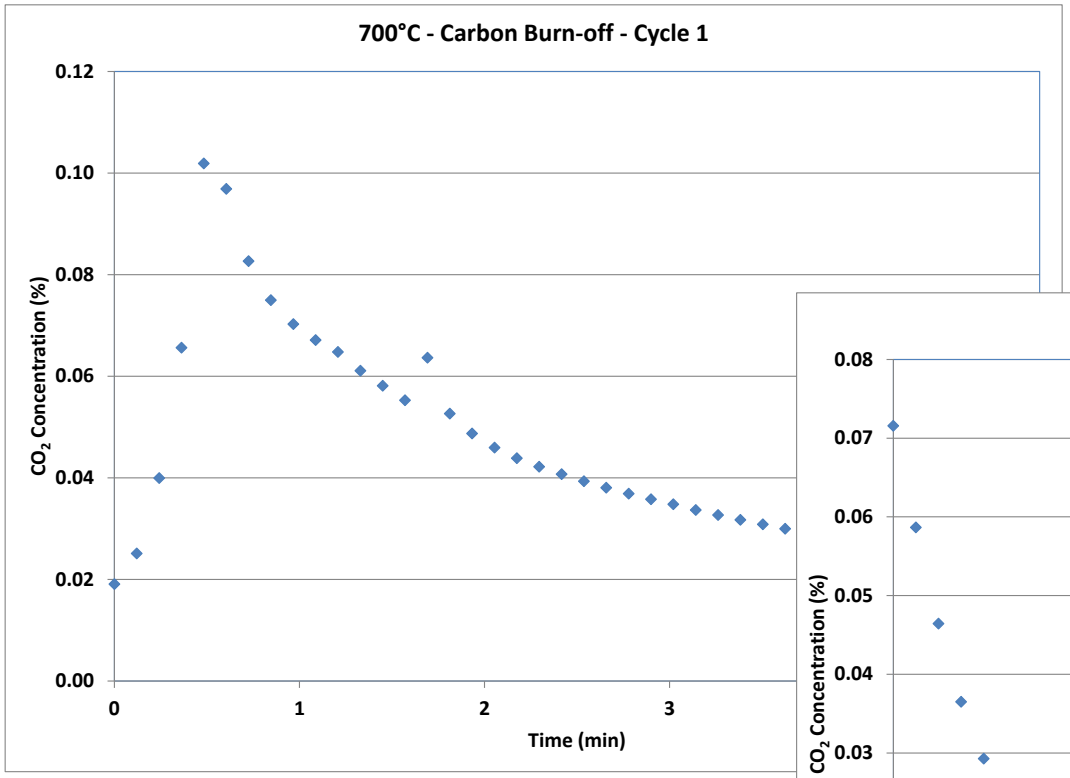

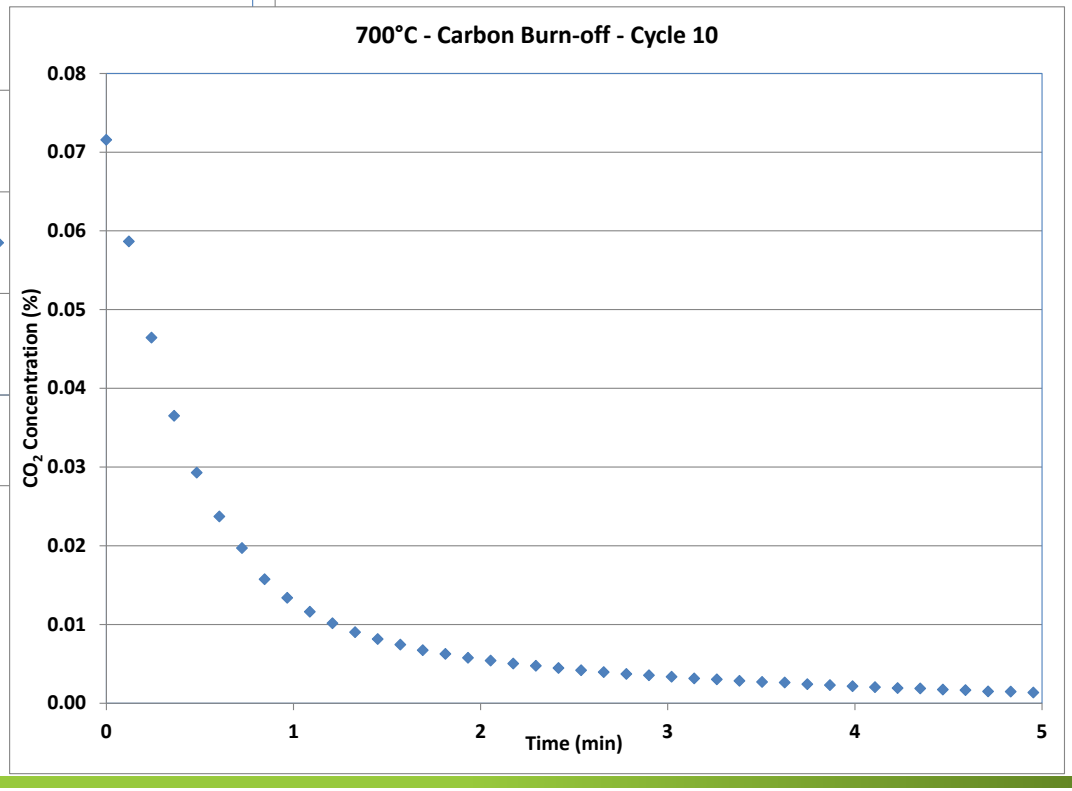

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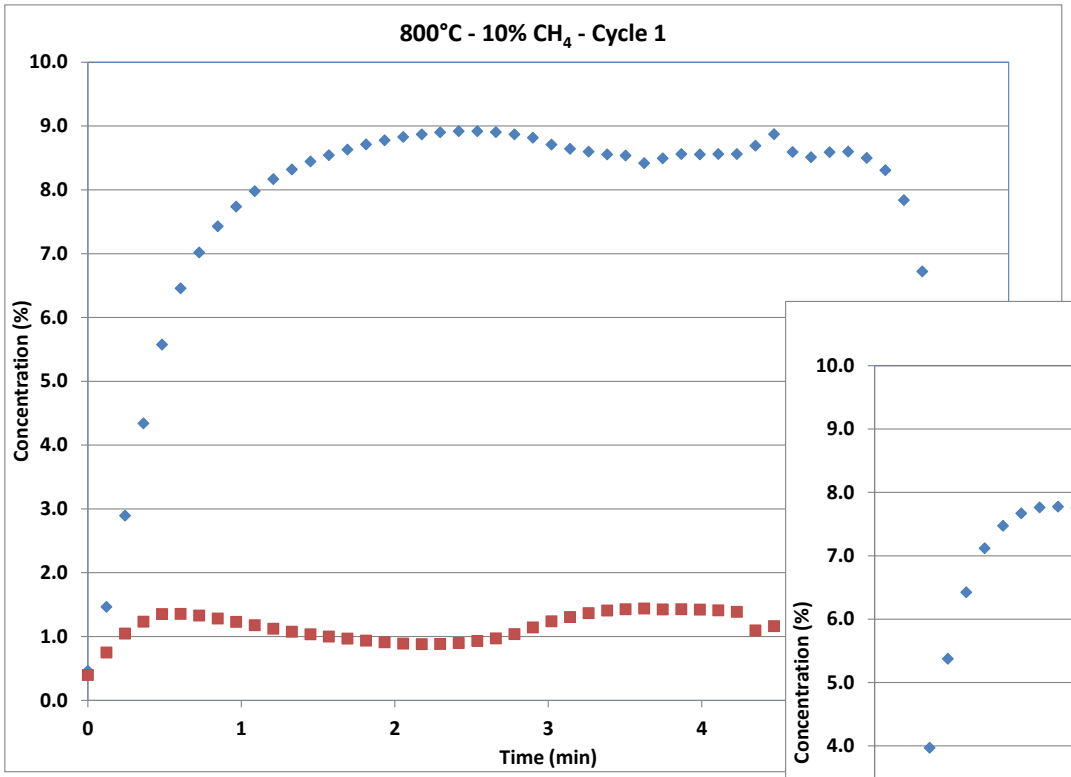

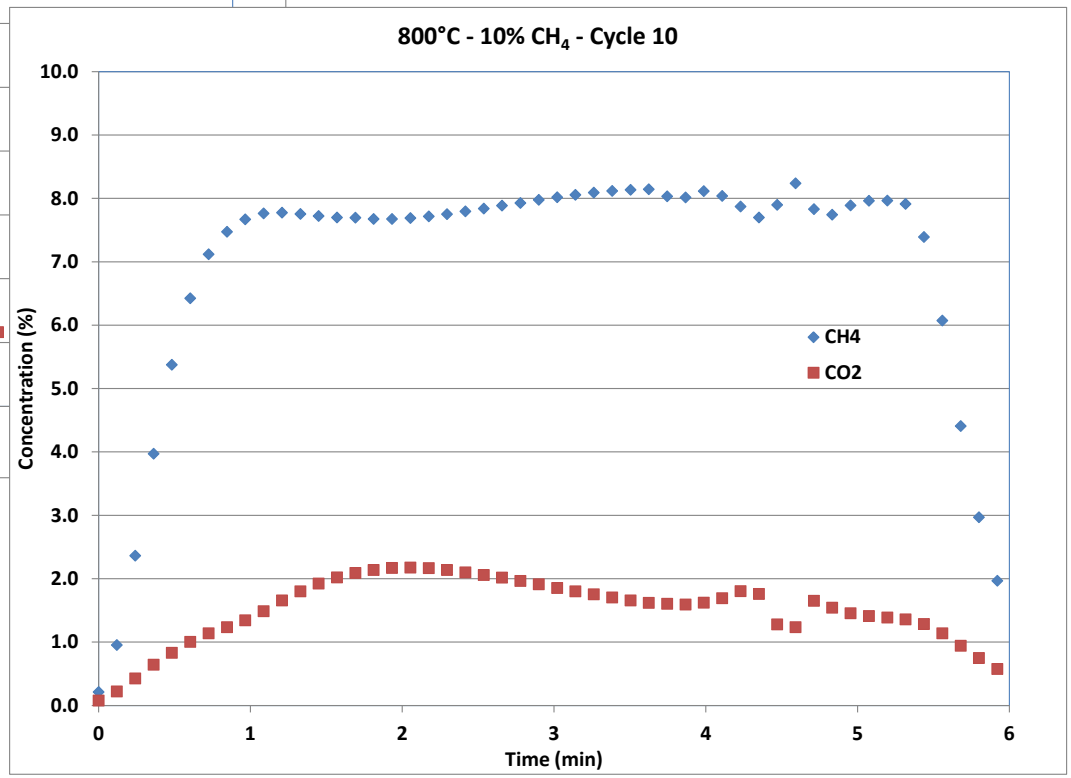

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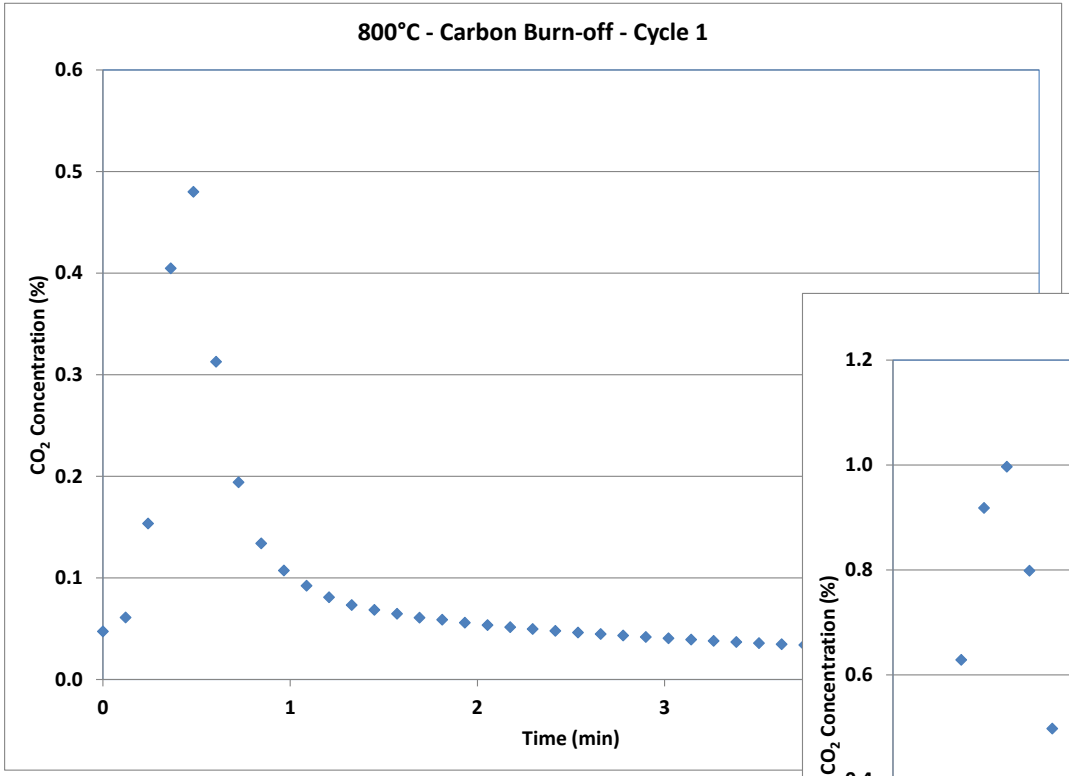

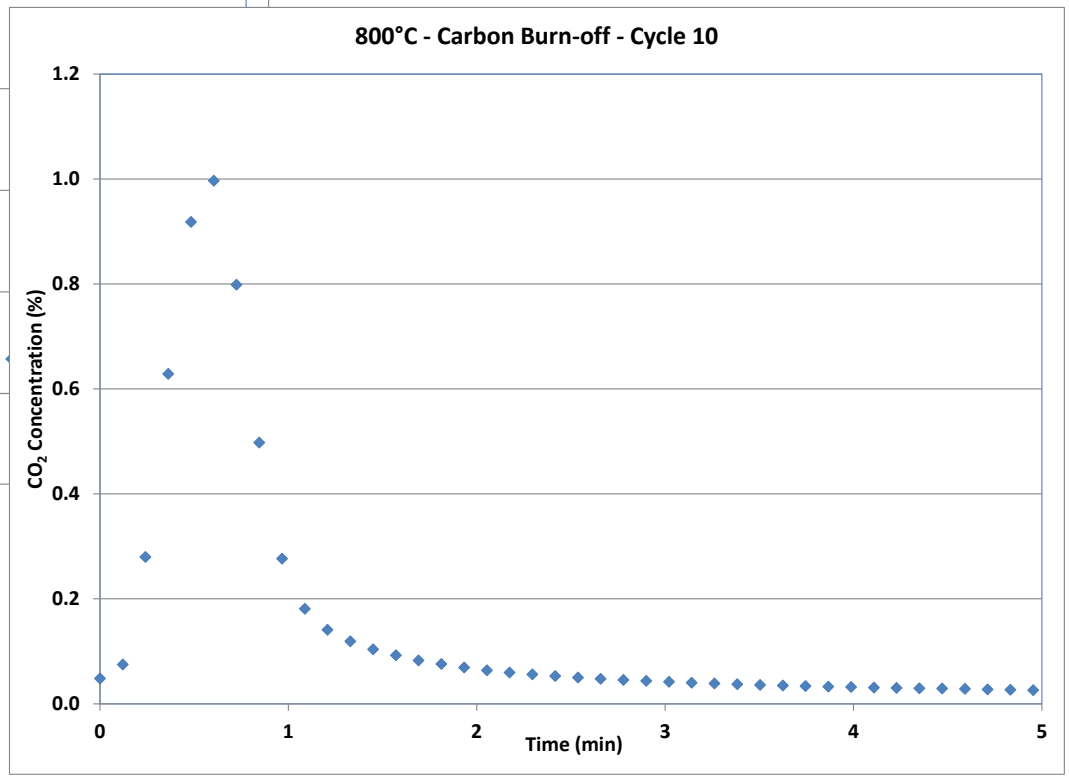

Hematite Reaction

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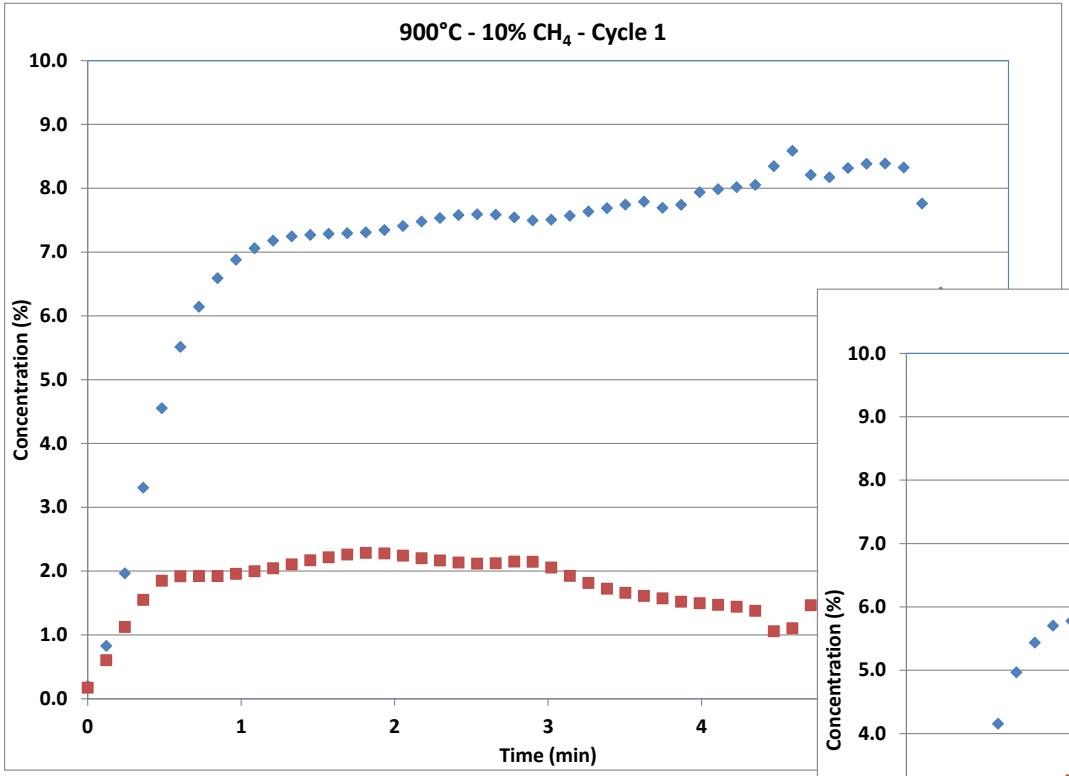
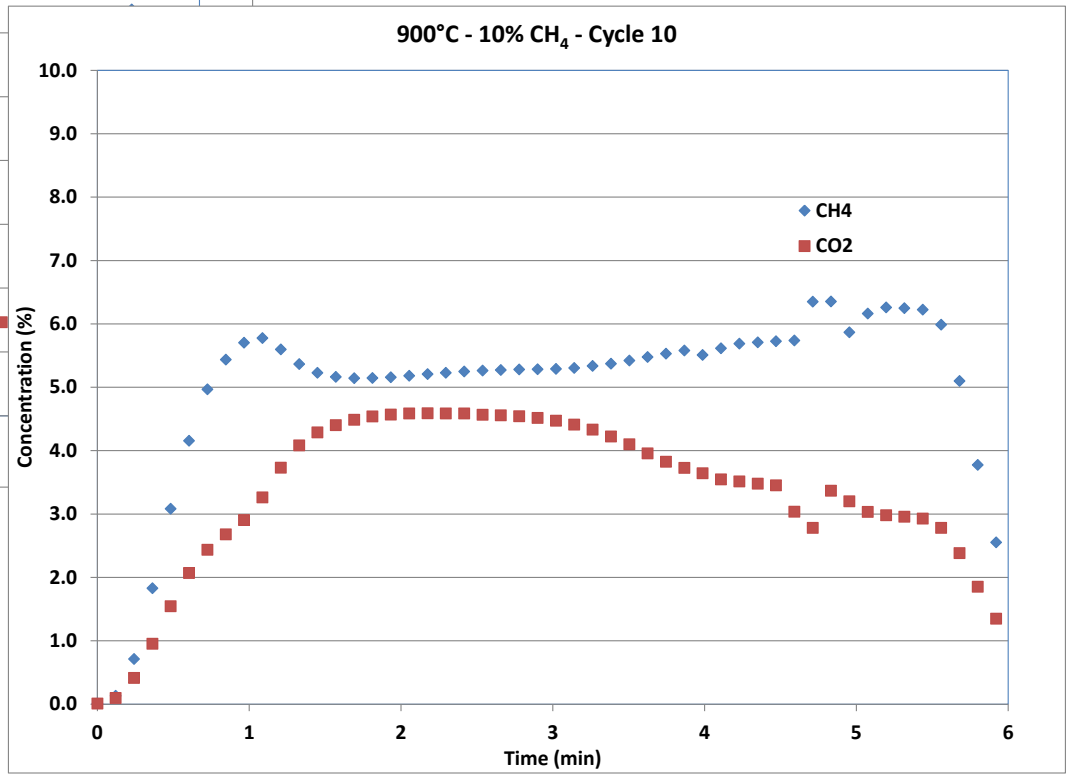
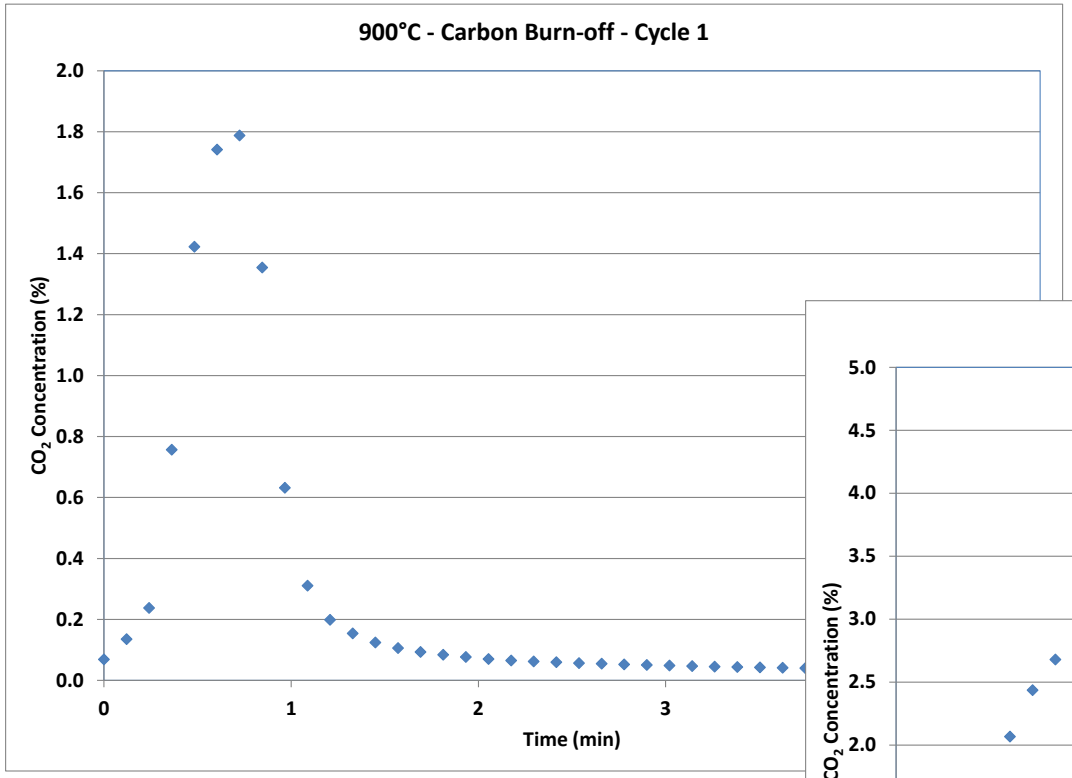
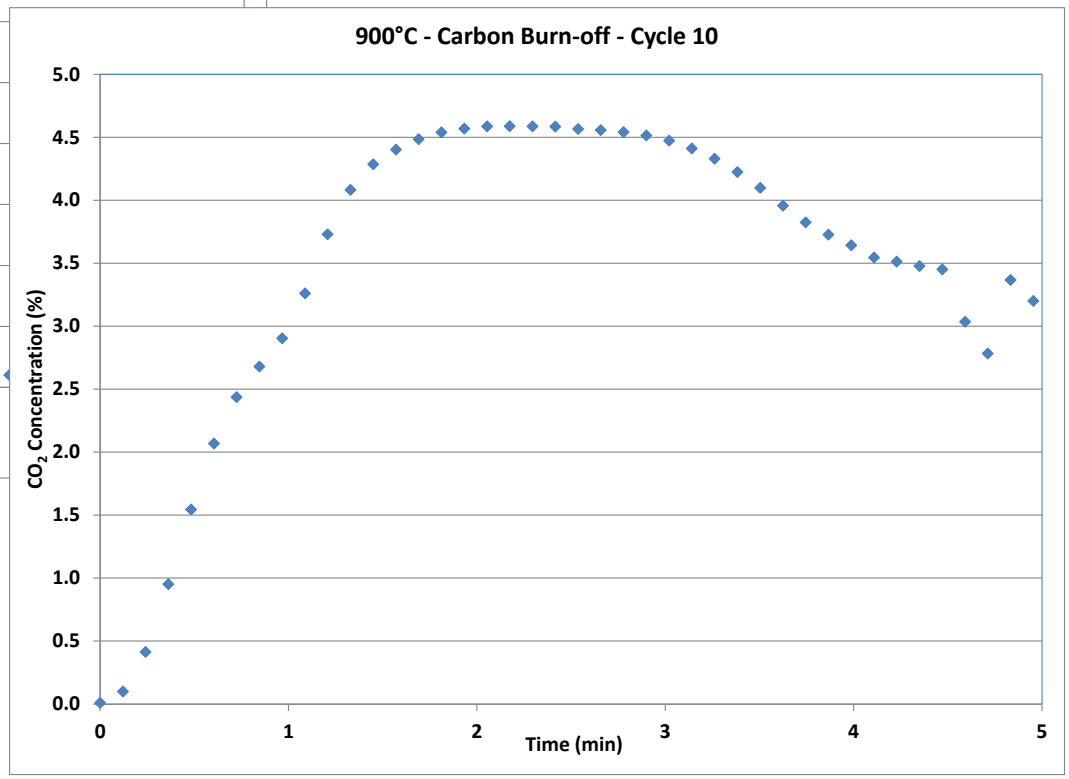




Hematite Reaction

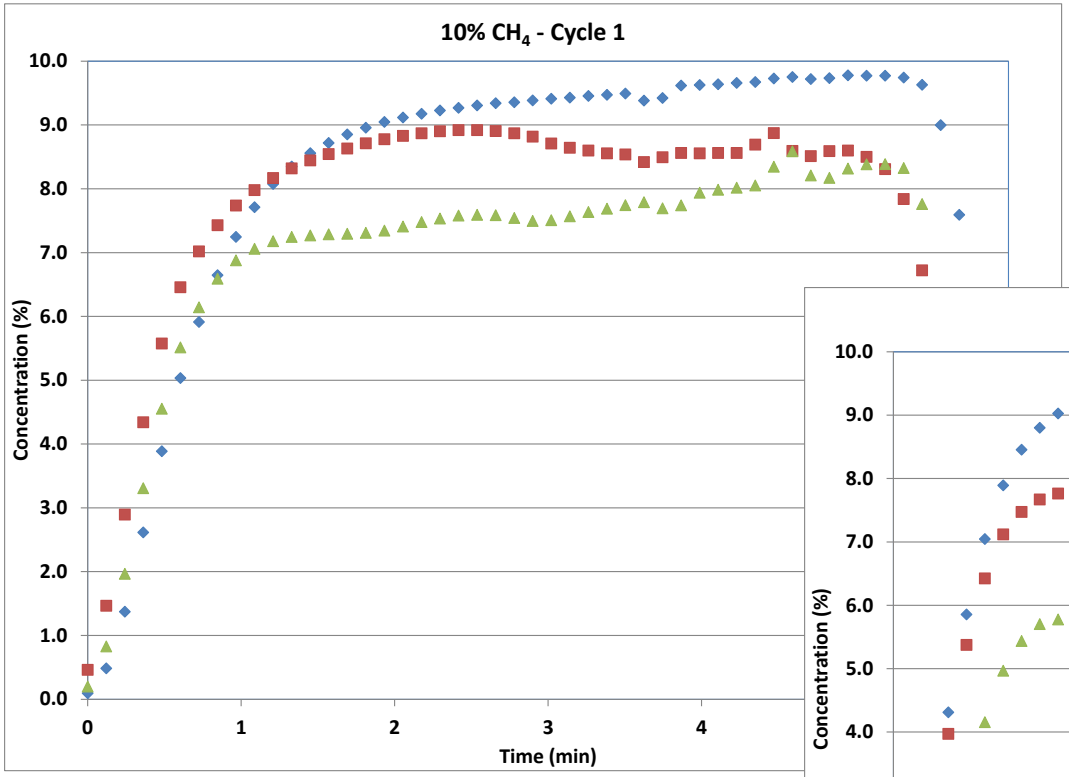
Multicycle CH4/Air Experiments

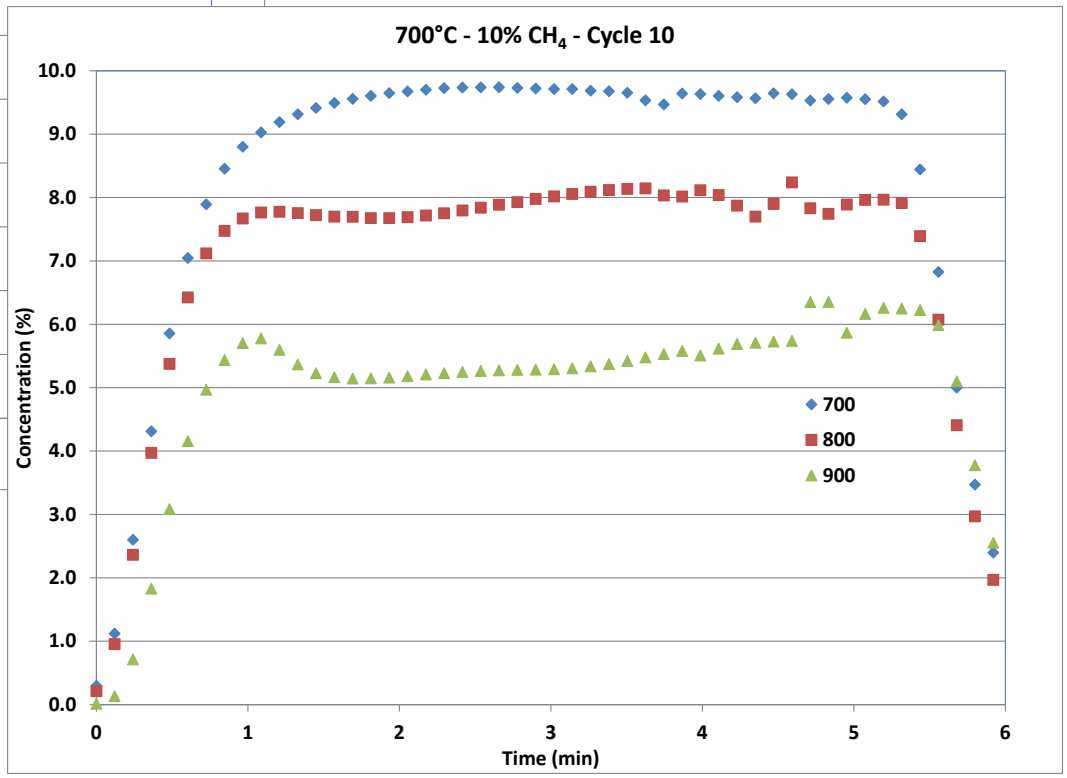




Hematite Reaction

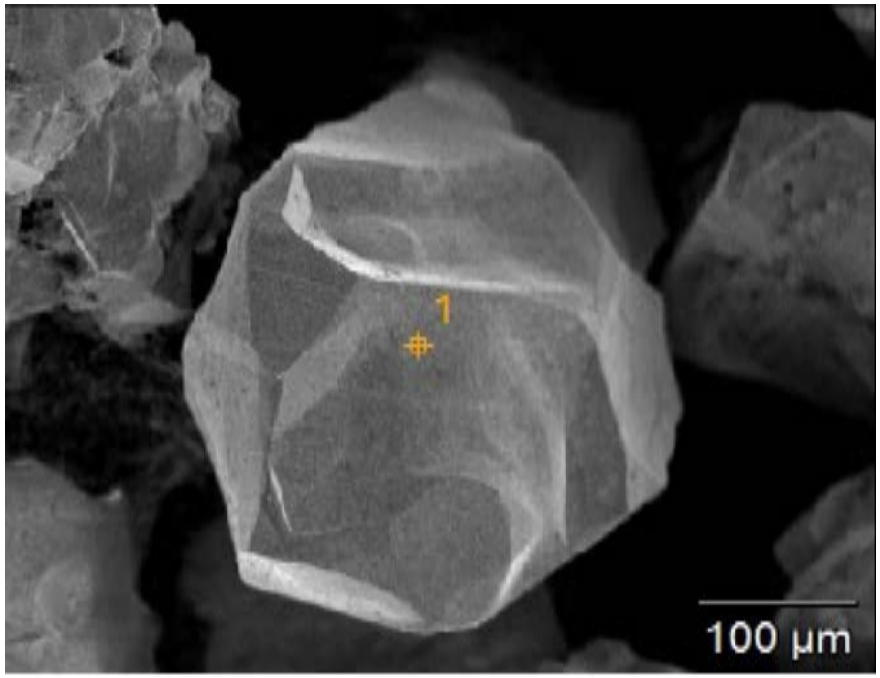
Multicycle CH4/Air Experiments

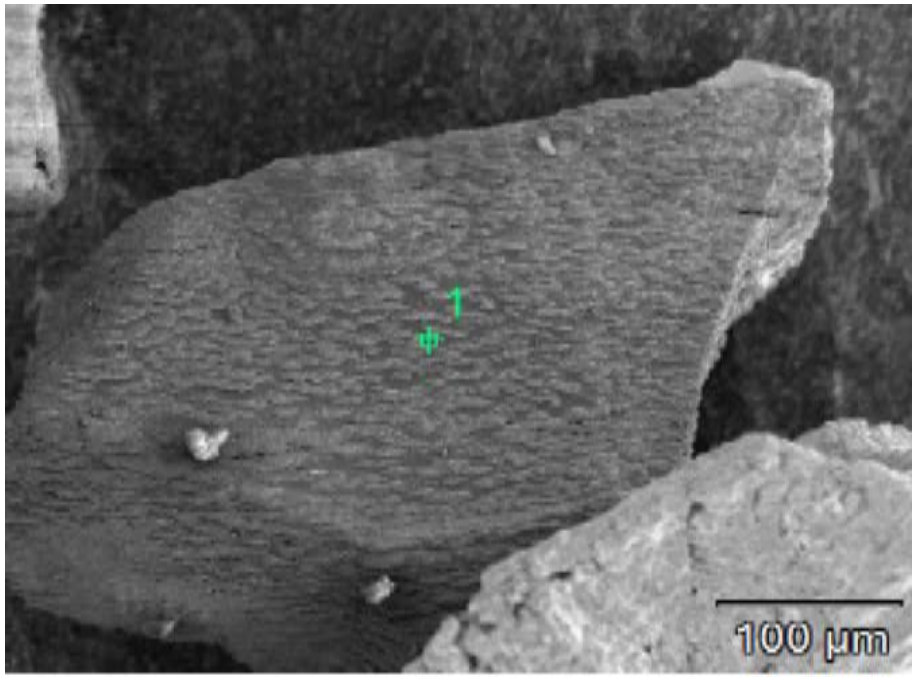




SEM/EDS Characterization

Fresh vs. Spent Hematite (900°C)





Fresh #	Fe (wt%)	Spent #	Fe (wt%)
1	68.9	1	73.9
2	62.3	2	63.2
3	60.3	3	70.8
Average	63.8	Average	69.3

Summary

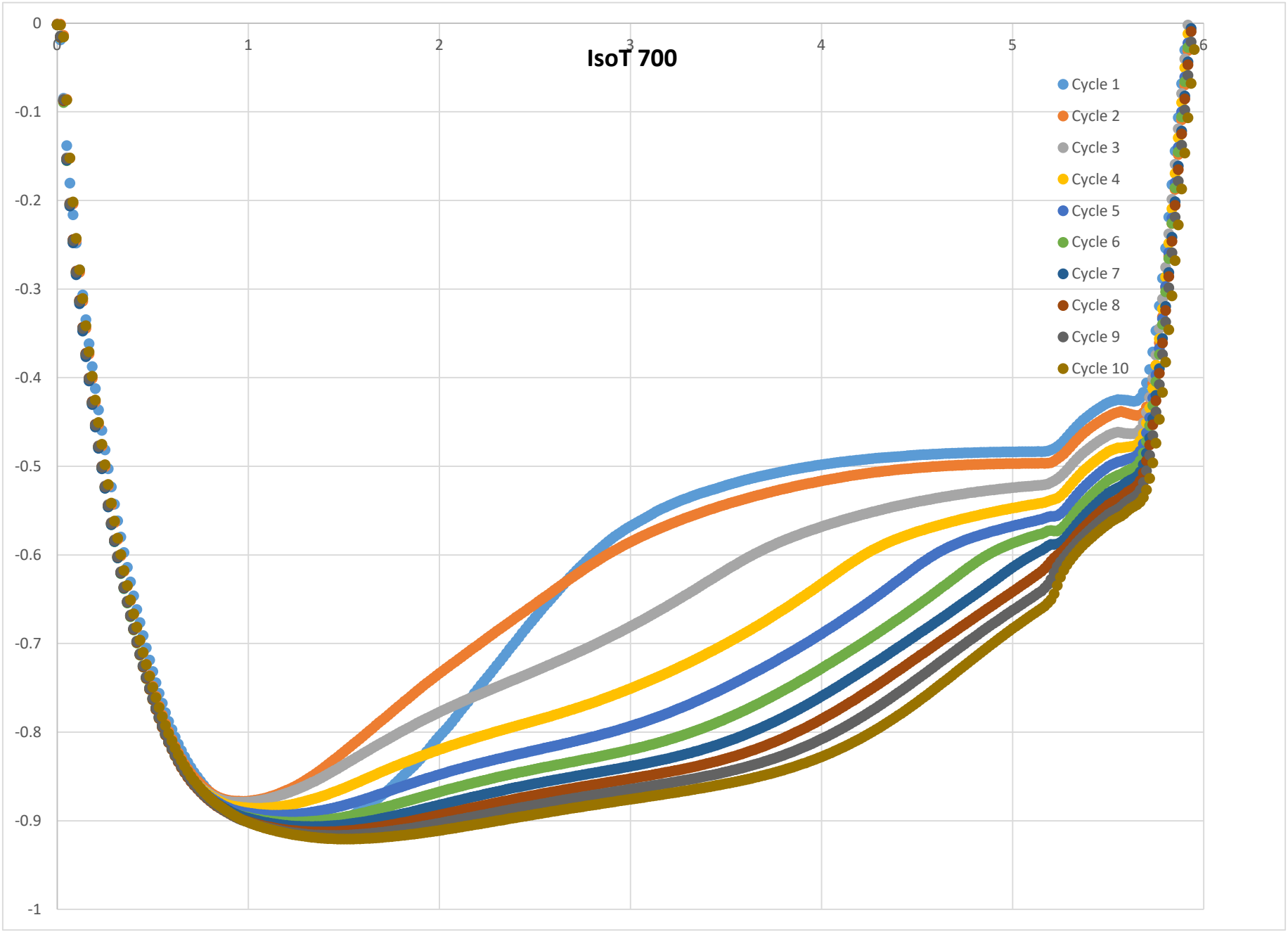
- Kinetic data set was generated for Canadian hematite OC from a series of multicycle fuel reaction/carrier oxidation experiments for use in CFD models
- OC reduction in hydrogen, followed by air oxidation, showed changes in reducibility over 10 cycles and with temperature
  - Increase in reduction only leveled off for 900°C within 10 cycles
- OC reaction with methane, followed by oxidation, showed an increase in conversion with temperature and number of cycles
  - Carbon accumulation observed for 900°C; incomplete burn-off with 5 min oxidation
- Surface concentration of Fe increased during the 10 cycle methane reaction experiments at 900°C
- Further variables to test: oxidation T and time, effect of product gases
- Deactivation kinetics still to be measured for model; must consider mechanical attrition
- Expand to fluidized bed and solid fuel experiments

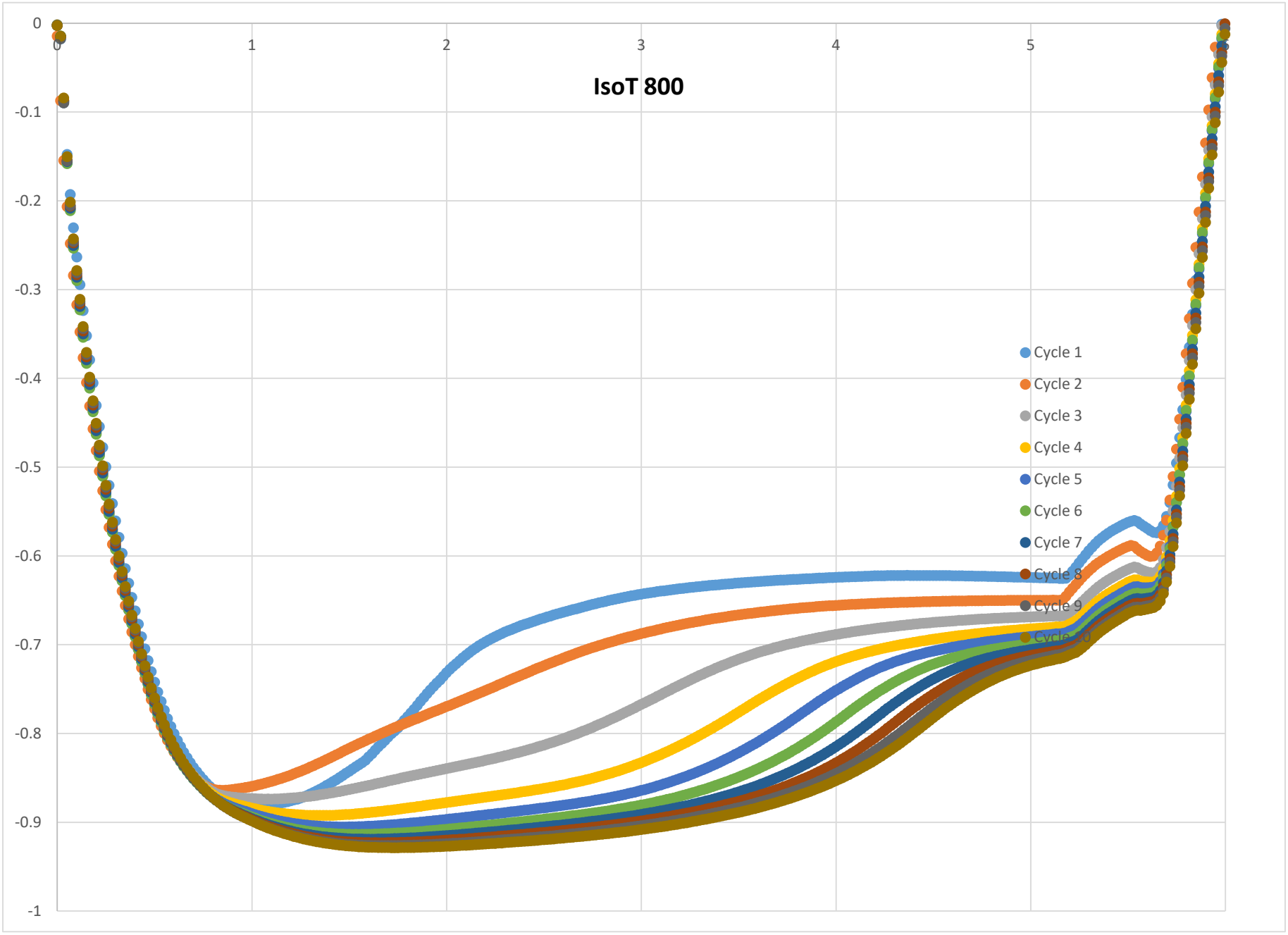
Acknowledgements

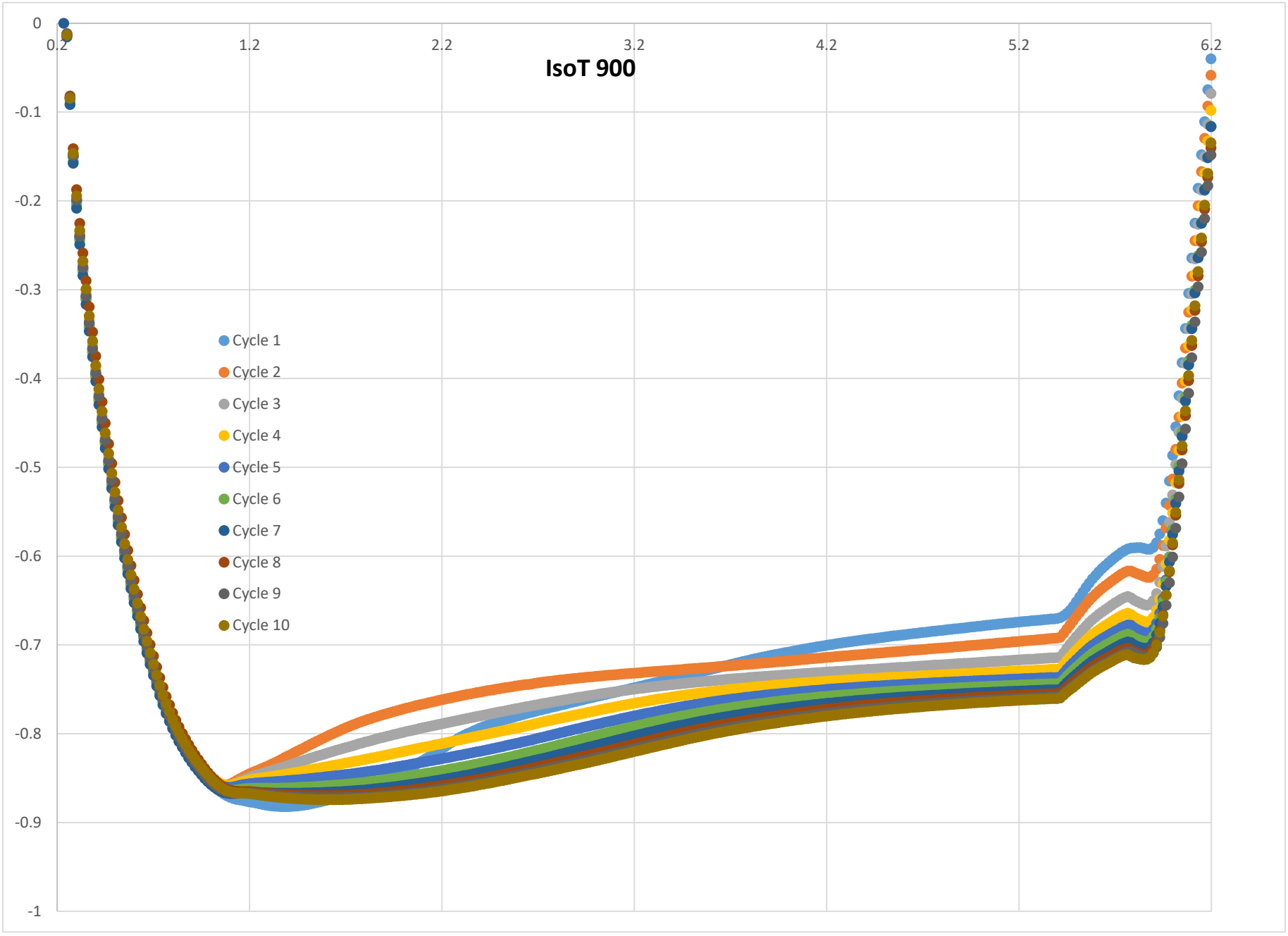
- Donald Floyd
- Matthew Dieterich

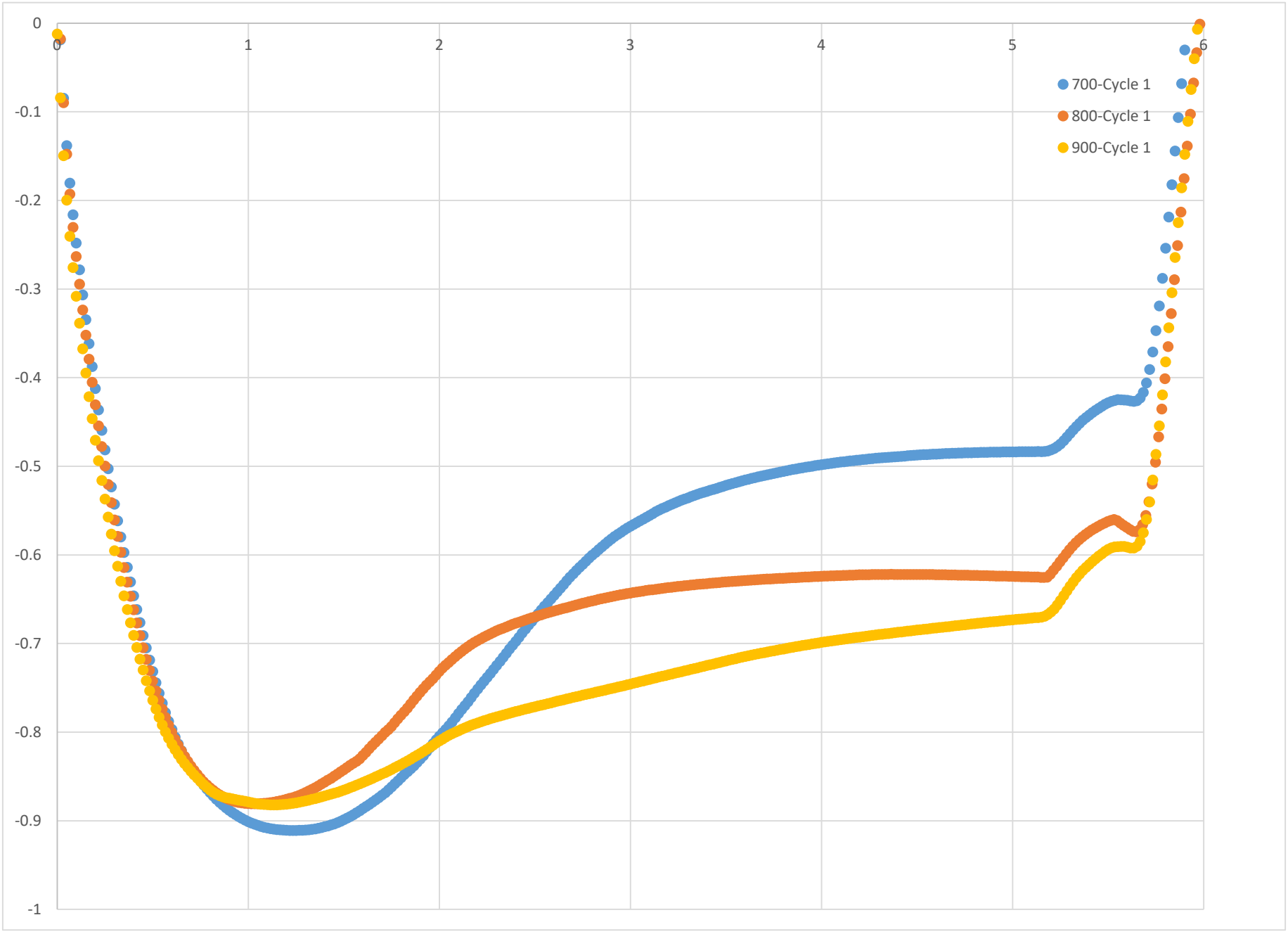

Thank you.
Questions?

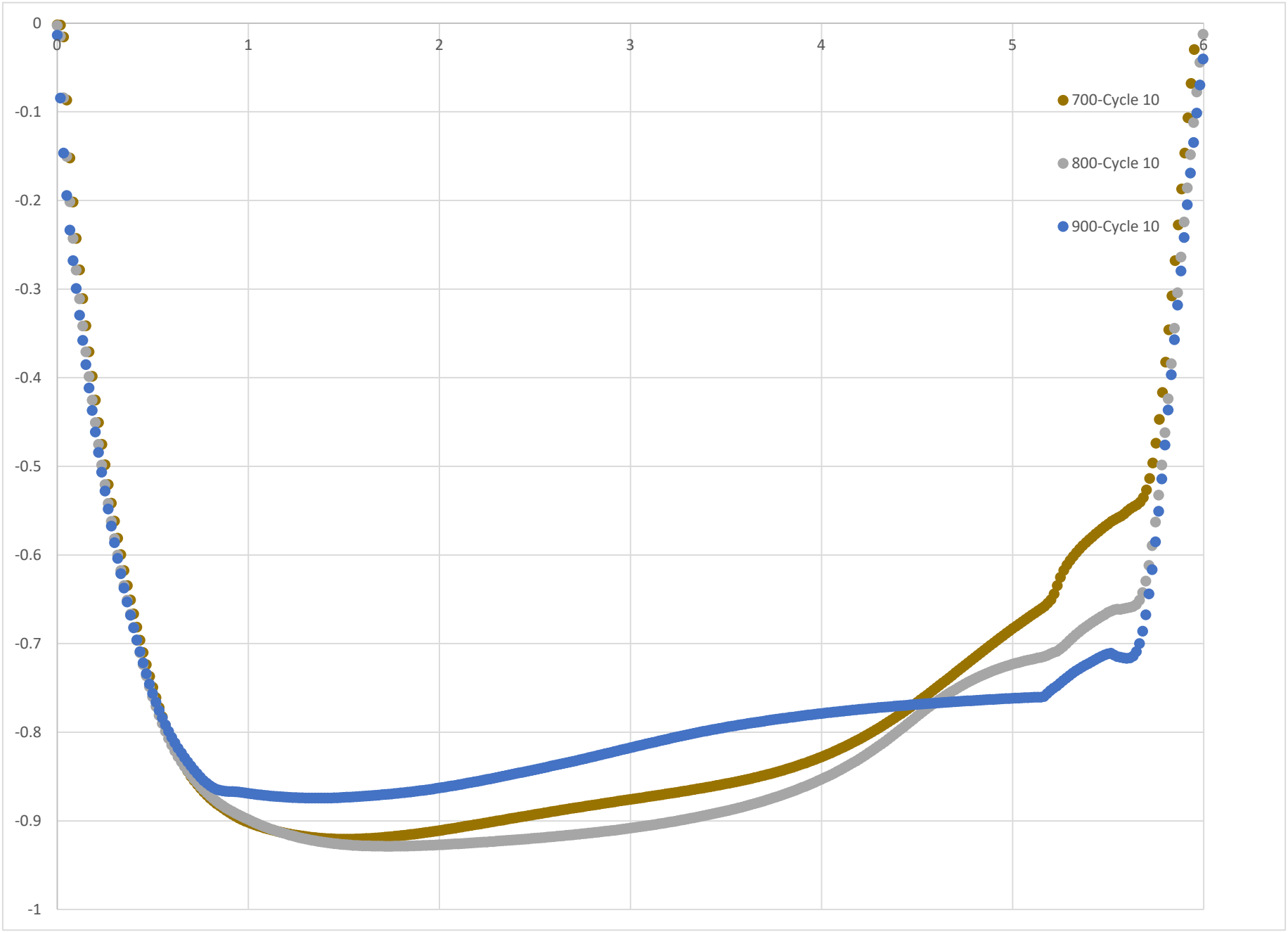
Other Slides

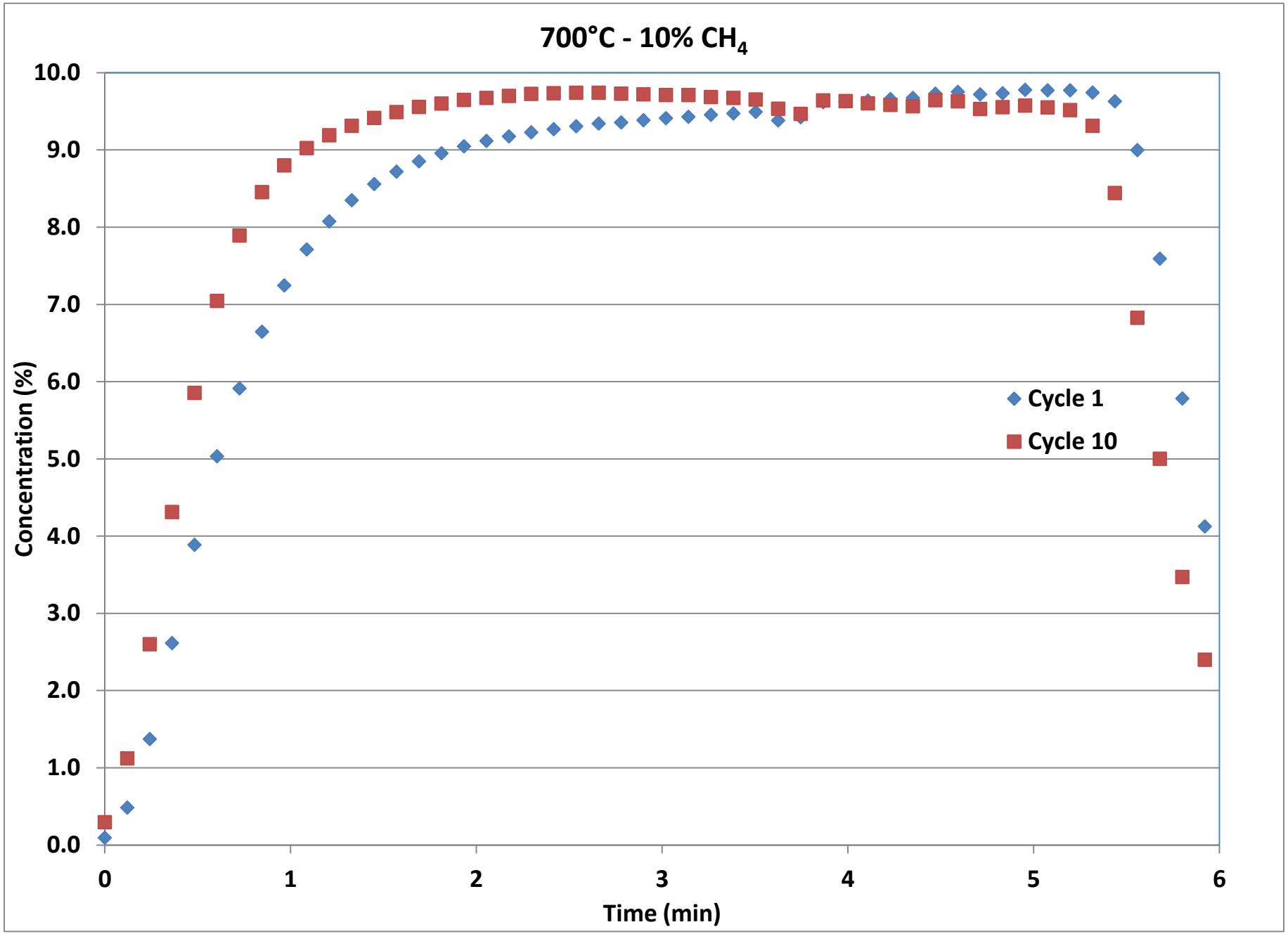

IsoT 700
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
1
2
3
4
5
6
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Cycle 6
Cycle 7
Cycle 8
Cycle 9
Cycle 10

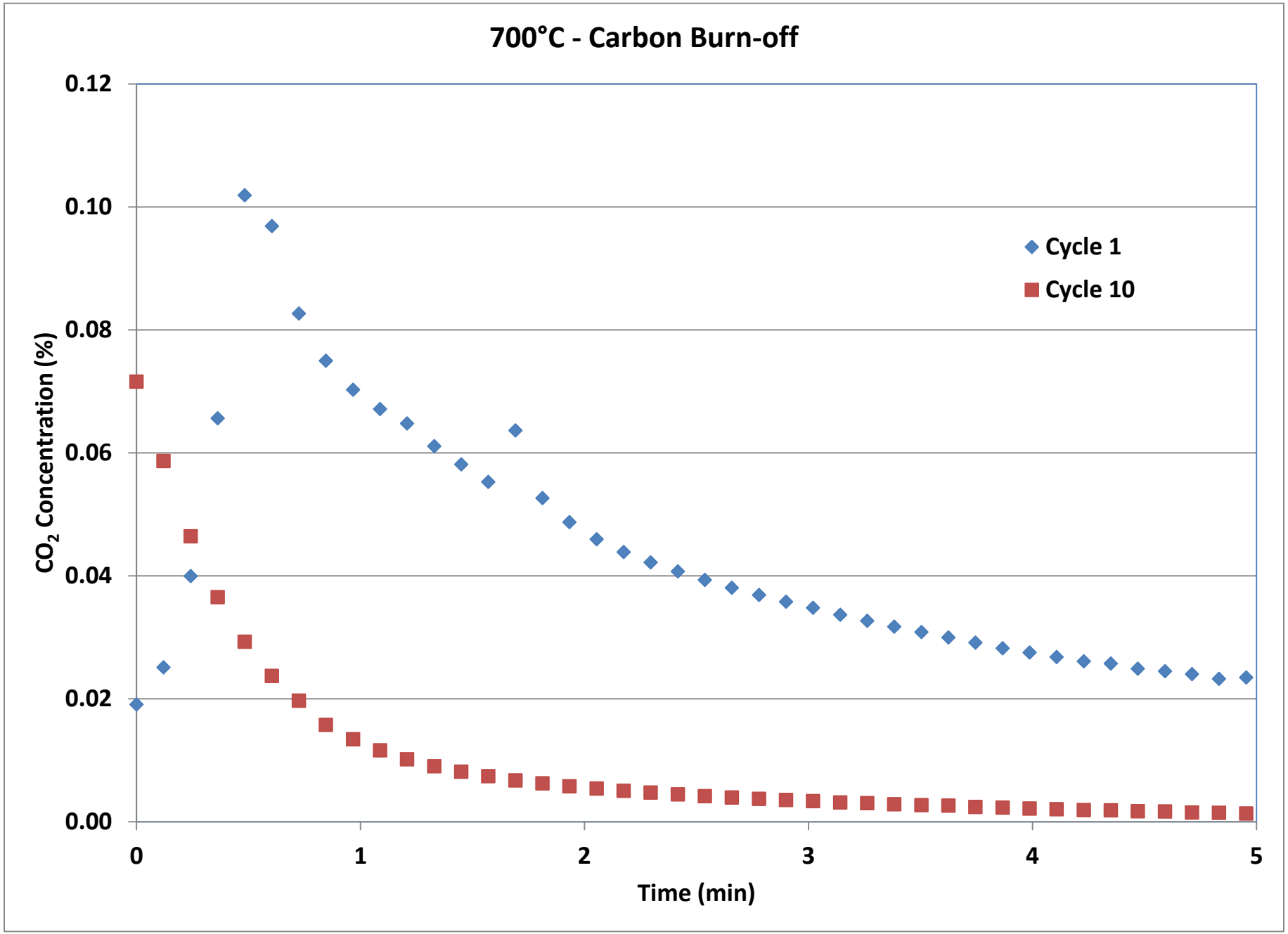

IsoT 800
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
1
2
3
4
5
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Cycle 6
Cycle 7
Cycle 8
Cycle 9
Cycle 10

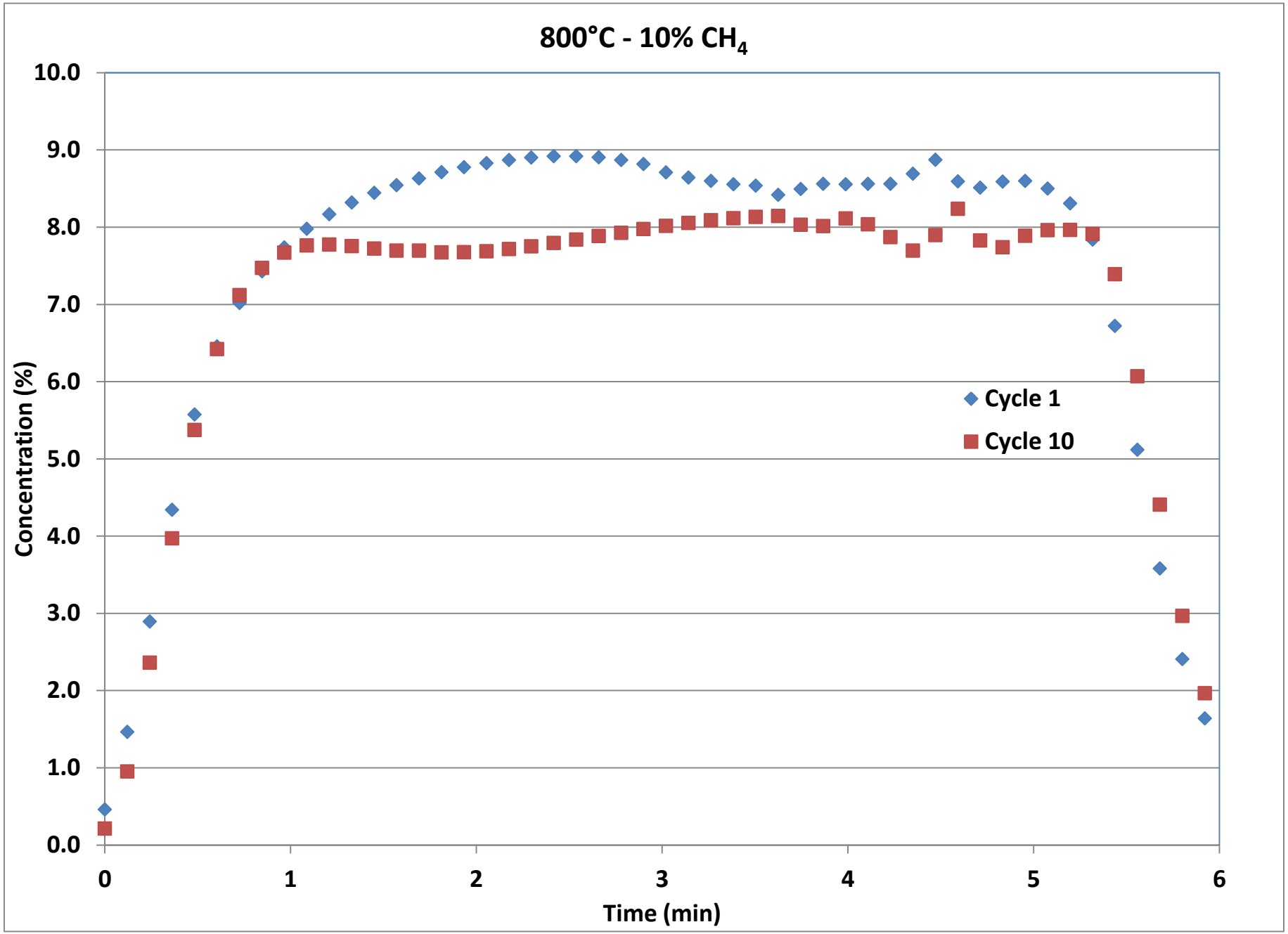

IsoT 900
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0.2
1.2
2.2
3.2
4.2
5.2
6.2
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Cycle 6
Cycle 7
Cycle 8
Cycle 9
Cycle 10

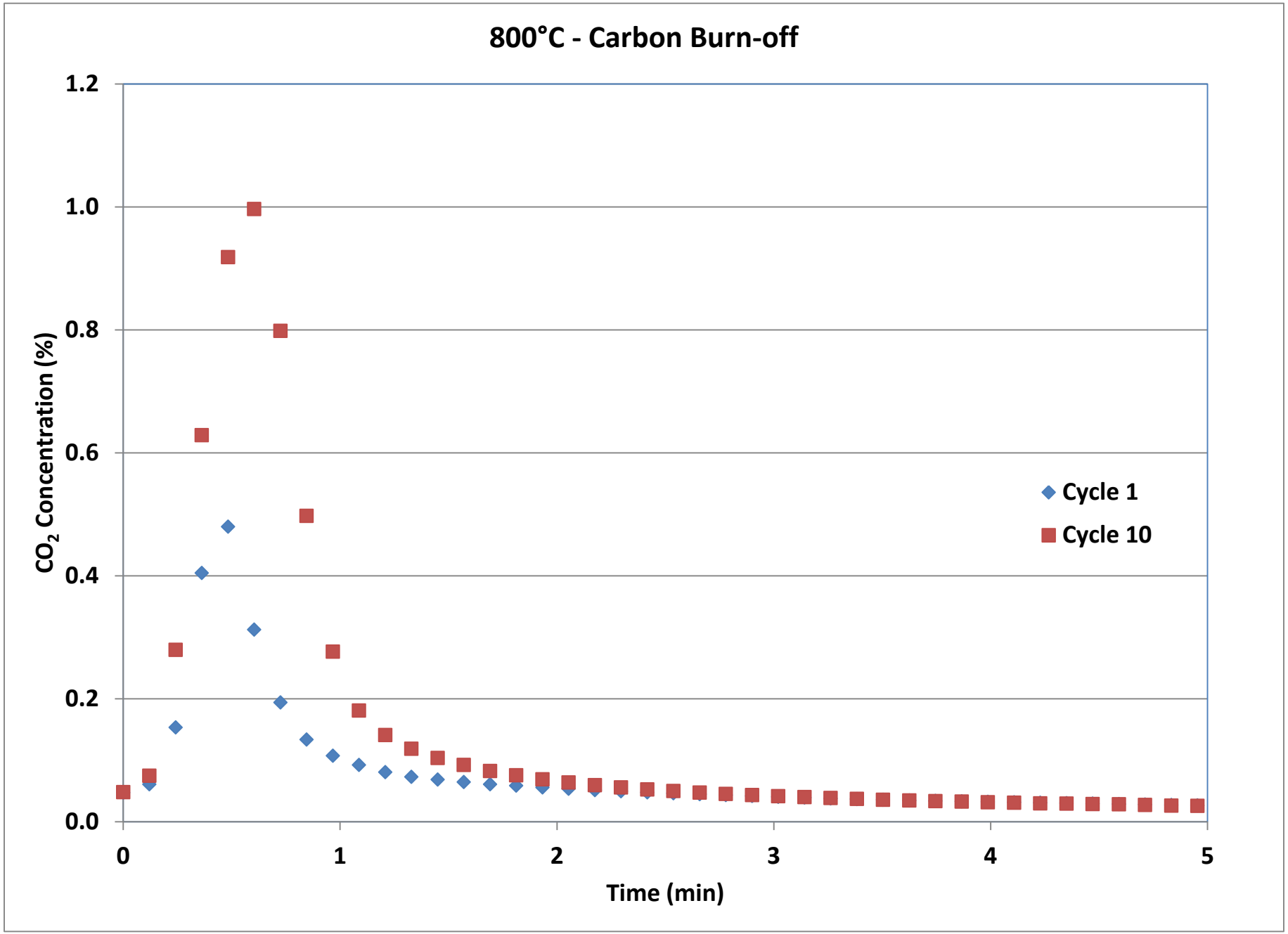

0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
1
2
3
4
5
6
700-Cycle 1
800-Cycle 1
900-Cycle 1

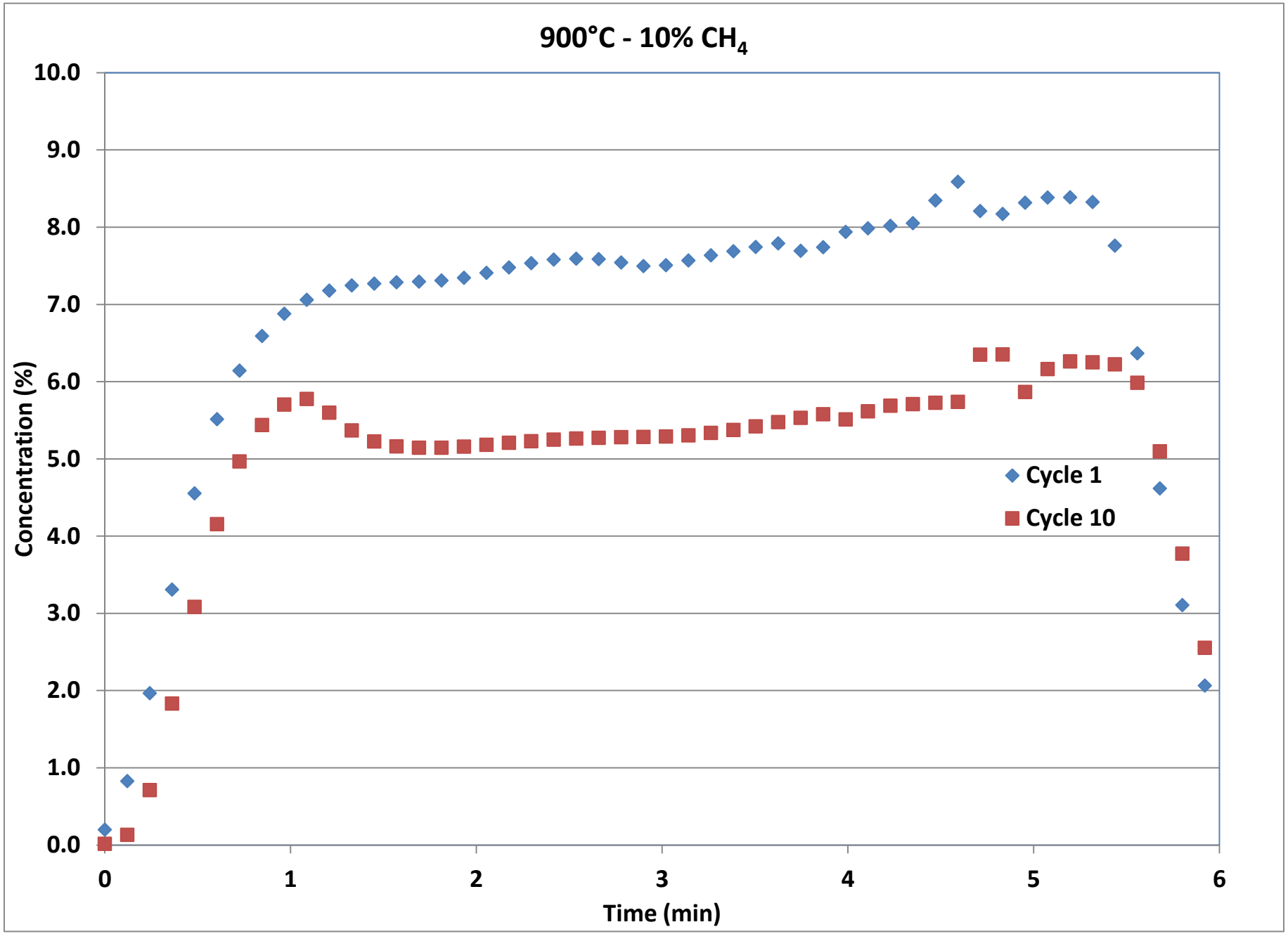

0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
1
2
3
4
5
6
700-Cycle 10
800-Cycle 10
900-Cycle 10

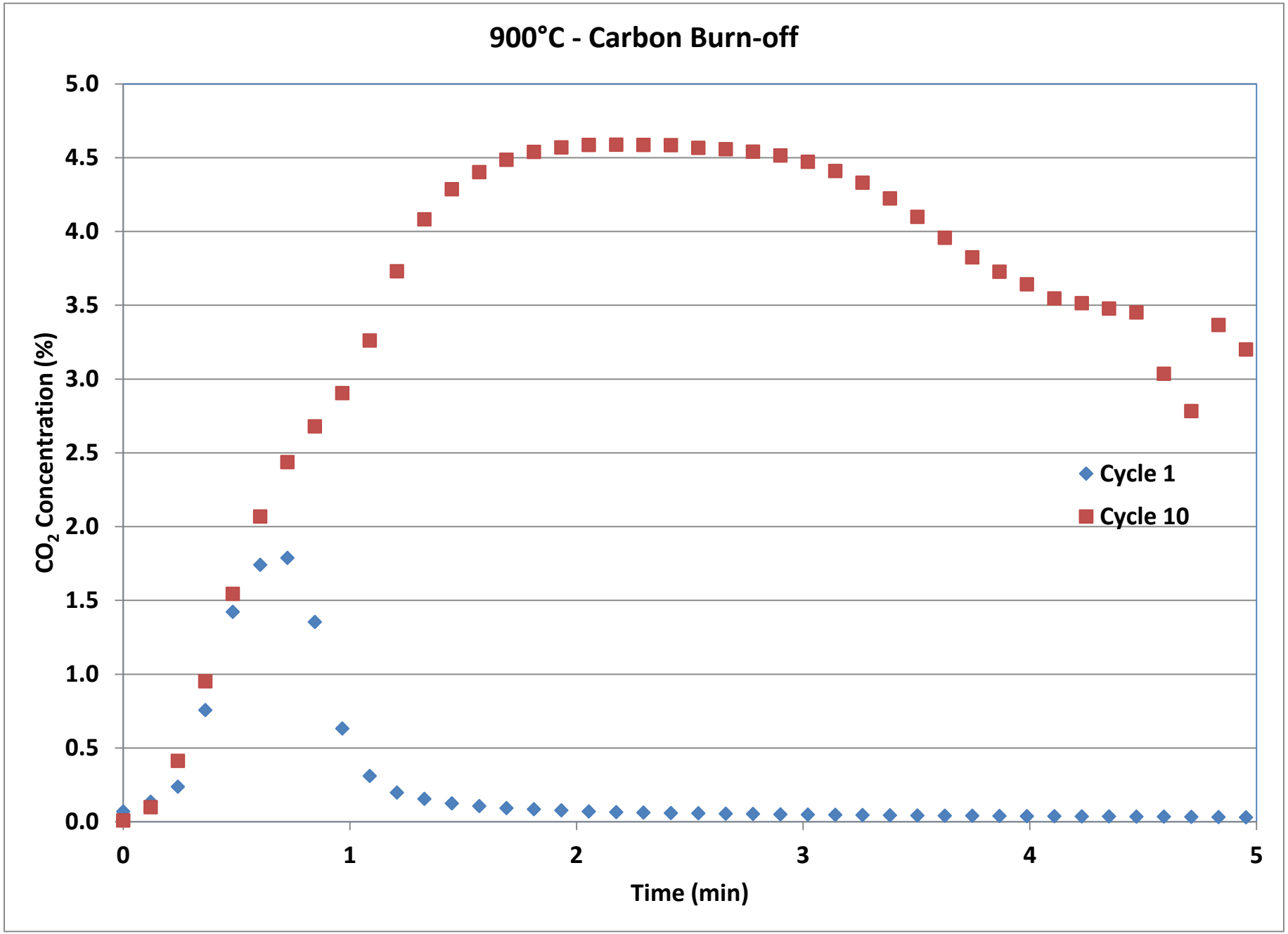

700°C - 10% CH4
Concentration (%)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
1
2
3
4
5
6
Time (min)
Cycle 1
Cycle 10


700°C - Carbon Burn-off
0.12
0.10
0.08
0.06
0.04
0.02
0.00
CO_2 Concentration (%)
0
1
2
3
4
5
Time (min)
Cycle 1
Cycle 10


800°C - 10% CH4
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Concentration (%)
0
1
2
3
4
5
6
Time (min)
Cycle 1
Cycle 10


800°C - Carbon Burn-off
1.2
1.0
0.8
0.6
0.4
0.2
0.0
CO_2 Concentration (%)
0
1
2
3
4
5
Time (min)
Cycle 1
Cycle 10


900°C - 10% CH4
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Concentration (%)
0
1
2
3
4
5
6
Time (min)
Cycle 1
Cycle 10


900°C - Carbon Burn-off
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
CO_2 Concentration (%)
0
1
2
3
4
5
Time (min)
Cycle 1
Cycle 10

Hematite Reaction

Multicycle CH4/Air Experiments

	Fresh	Spent		ICP
1	68.90701	73.87923		57.27
2	62.27045	63.1886		
3	60.28093	70.75227		
	63.81946	69.27337		

BACKGROUND/MOTIVATION

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  - EPA Clean Power Plan targets 30% reduction by 2030
  - 85% reduction by 2050
- Fossil fuels are important for domestic energy security and reliability
- Options to reduce GHGs for fossil fuels are needed
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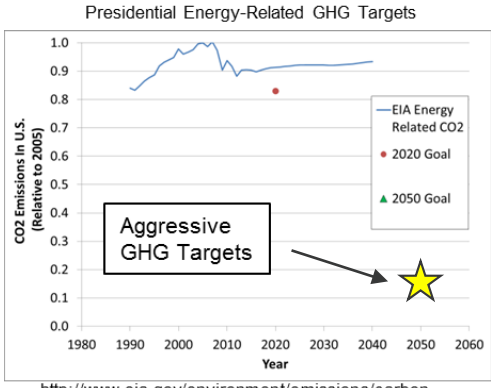

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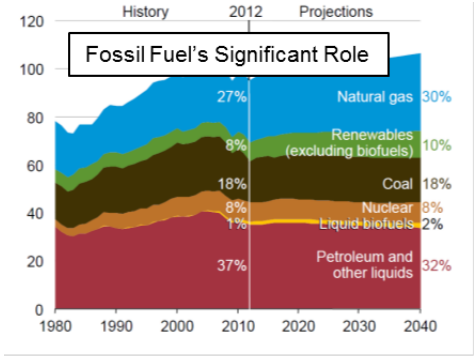

AEO2014 – Early Release

ADV. COMBUSTION – WHY IS NETL/RIC DOING THIS WORK?

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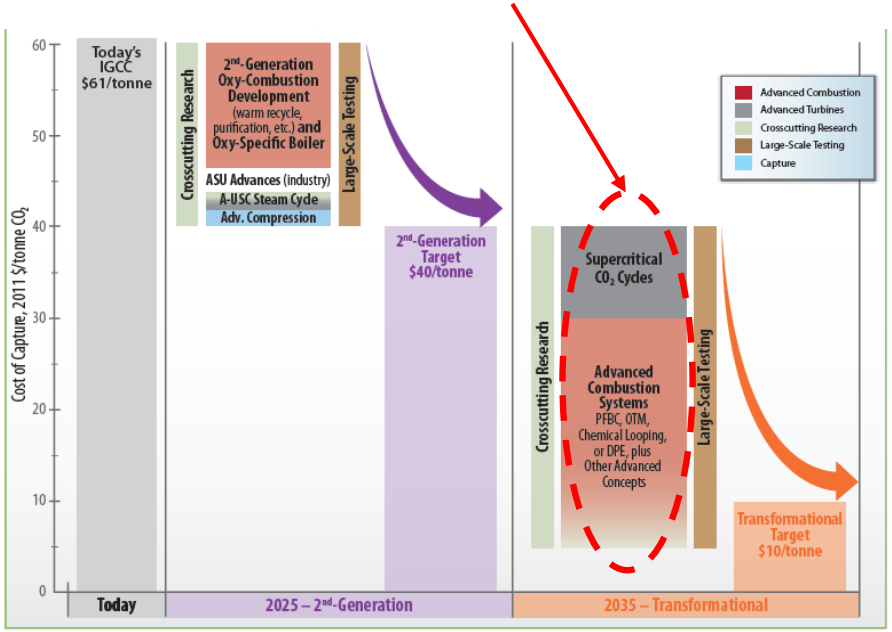

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ADVANCED COMBUSTION: CLC – WHERE ARE WE NOW?

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  - 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
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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