Development of Oxygen Carriers for Coal Conversion to Syngas

NATIONAL ENERGY TECHNOLOGY LABORATORY

Jonathan W. Lekse and Ranjani Siriwardane

Gasification Systems Meeting, April 9, 2019

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Advanced Reaction Systems

Project Goal

- **Challenge: Develop modular small-scale energy conversion with low emissions, high reliability, low cost of product, and flexibility to respond to a myriad of niche opportunities.**
  - Needs built around interchangeable components – facilitates upgrades at the component level as new technologies mature
  - Low cost technology via mass production in lieu of large scale
  - Low emissions including CO_2
  - Support a portfolio of component technologies – Enables Energy Conversion designs optimized for local niche opportunities (e.g., coal type, biomass, unique consumer needs)
  - Provide framework for researchers to offer continuous improvement in costs, emissions, and flexibility via Radical Engineering – leveraging advances in manufacturing, simulation, and maturation of advanced technologies at reduced development time and cost

Advanced Reaction Systems

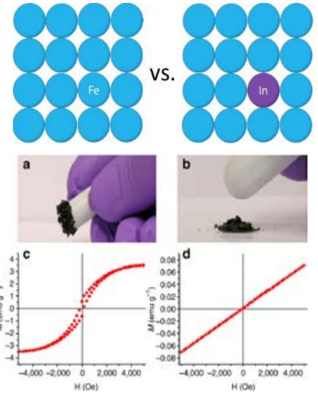
New Approach - Tasks

- Task 1 – Project Coordination/Management
- Task 2 – Gasification Test Facility
- Task 3 – Advanced Gasifier Design
- Task 4 – Advanced Manufacturing Technologies for Gasification
- Task 5 – Oxygen Production for Gasification
- Task 6 – Microwave Reactions for Gasification
- Task 7 – Non-Traditional Thermal Reactor Technologies
- Task 8 – Microbial Reactors for Gasification Systems
- Task 9 – MFiX Suite Multiphase Code Development, Validation, Application
- Task 10 – Machine Learning to Accelerate CFD Models

Oxygen Carrier Studies

Project Goals

- Guiding Principle
  - We want to understand how changes at an atomic level affect process performance and economics
- Specific goals
  - Investigate solid materials that can separate oxygen from air
  - Identify and understand how atomic level changes effect process scale properties
  - Design and synthesize oxygen carrier materials for specific applications
  - Design products and reactor systems that use solid carrier materials to deliver oxygen



Atomistic Studies
Property Testing

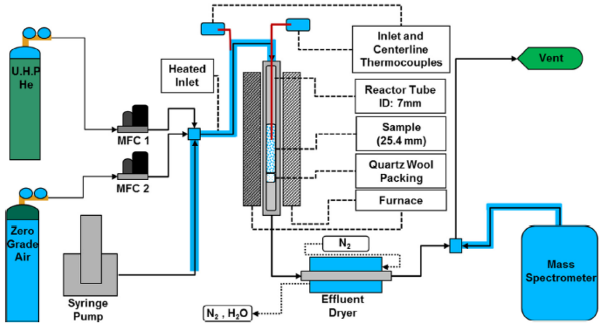


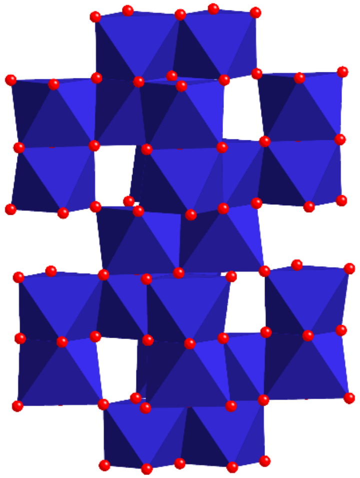
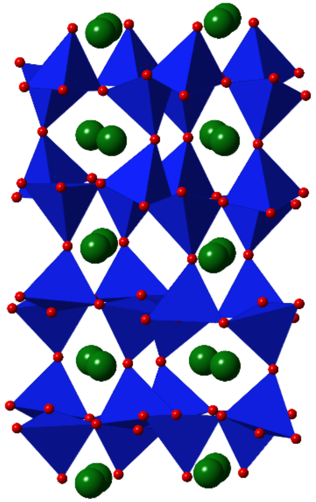
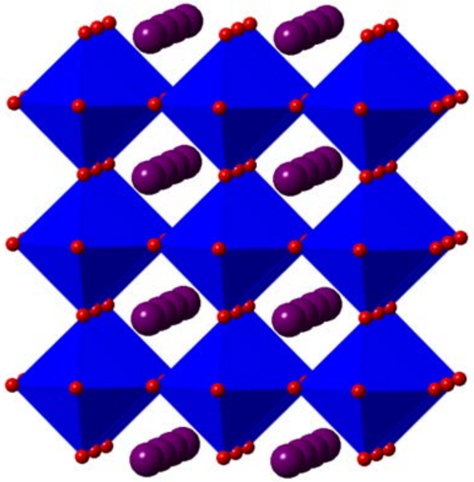
Fig. 4. Schematic of fixed bed reactor system.

Lab-Scale
Process Testing

Large-Scale Performance
and Economics

Oxygen Carrier Studies

Materials of Interest

Binary Oxides	Ferrites	Perovskites
		

Binary Oxides

- Inexpensive
- Can have good reactivity
- Limited operating temperature range
- Potential agglomeration

Ferrites

- Can be used for partial oxidation
- Ideal for gasification
- Compositional flexibility
- Stable

Perovskites

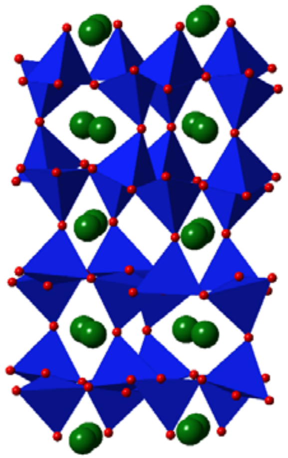
- Easily reduced/oxidized
- Compositional flexibility
- Tuneable oxygen capacity and temperature range
- Stable

Ferrite Carrier Materials

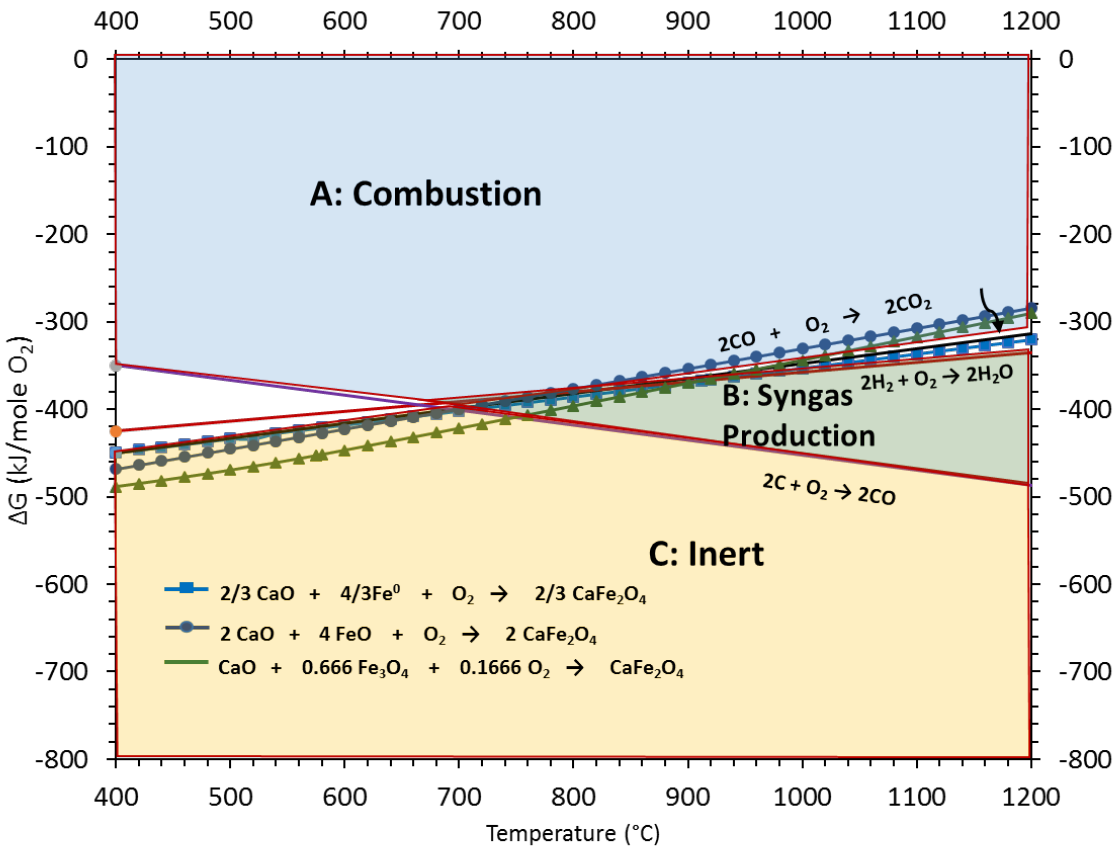
Overview

- Ferrites are a derived from iron oxides with many adopting the spinel or inverse spinel structures with a general formula of AFe_2O_4
  - Cubic Close Packed Oxygen Atoms
  - Spinel: A cations on 1/8 of tetrahedral holes and B cations on ½ of octahedral holes
  - Inverse Spinel: B cations on 1/8 of tetrahedral holes, A cations on ¼ of octahedral holes, B cations on ¼ of octahedral holes
- The A cation in these structures can be a wide variety of 2+ cations and significantly impact the properties of the resulting material

- Applications
  - Magnets and Ferrite Cores
  - Ferrite Beads
  - Inductors
  - Transformers
  - Electromagnets
  - Oxygen Carriers



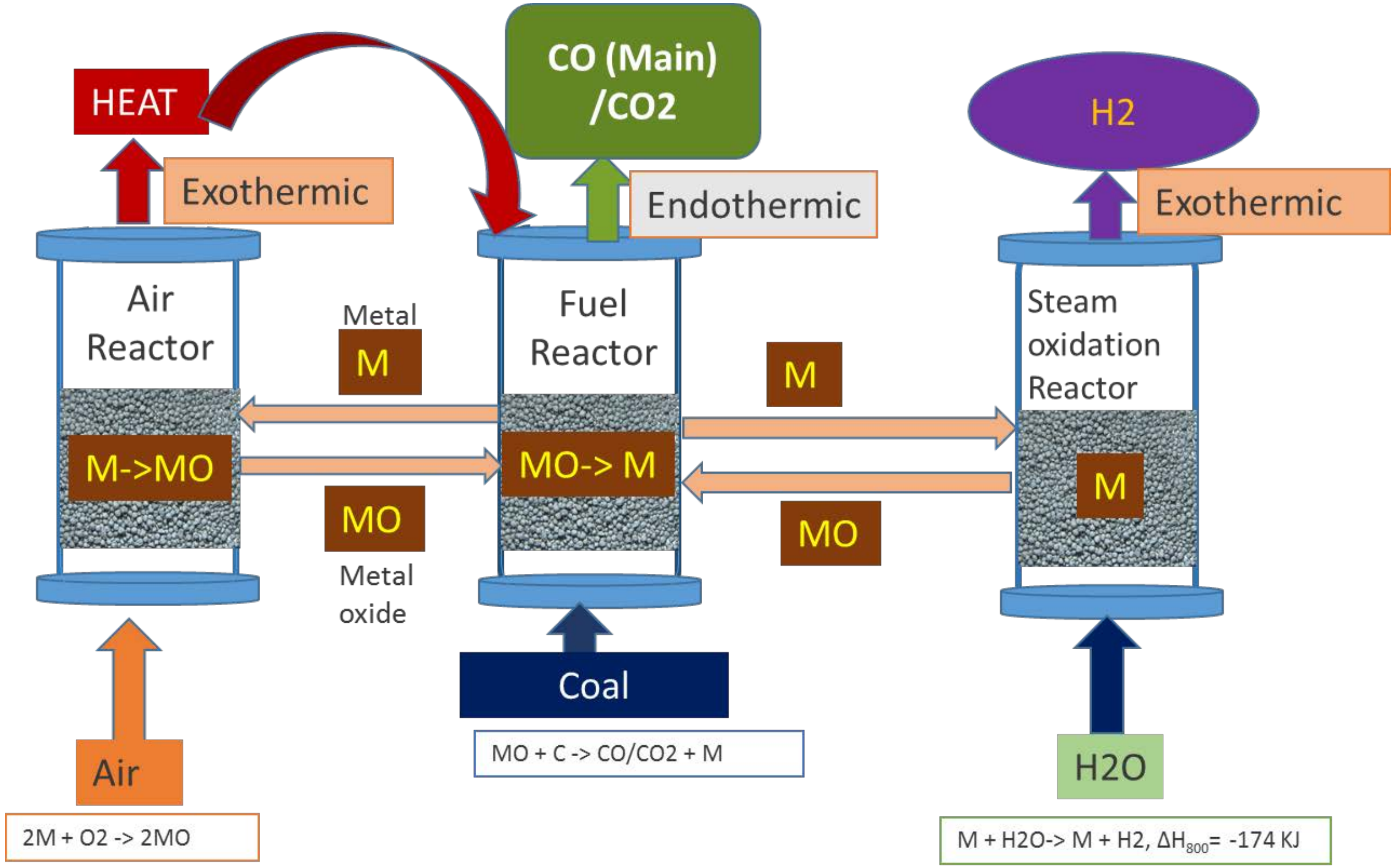
Spinel Ferrite



Modified Ellingham diagram for $CaFe_2O_4$ at 700-850 ^0C[1]

Ferrite Carrier Materials

Process Overview

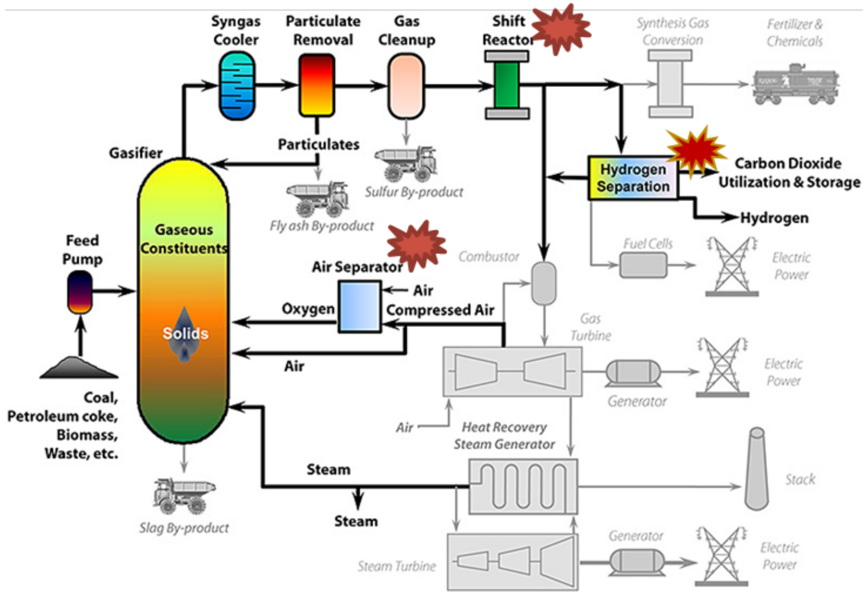


- Novel mixed metal oxide oxygen carriers (MO) have unique characteristics
  - They directly react with coal to produce CO (no full combustion)
  - Reduced metal ferrite can be oxidized with steam to produce H2
- Fuel reactor: Coal reacts directly with MO to produce reduced metal oxide and CO (useful product)
- Steam oxidation reactor : Reduced metal (M) is oxidized with steam to produce pure H_2. Reaction is exothermic.
- Air reactor: Reduced oxygen carrier is oxidized with air to generate heat for the fuel reactor

Ferrite Carrier Materials

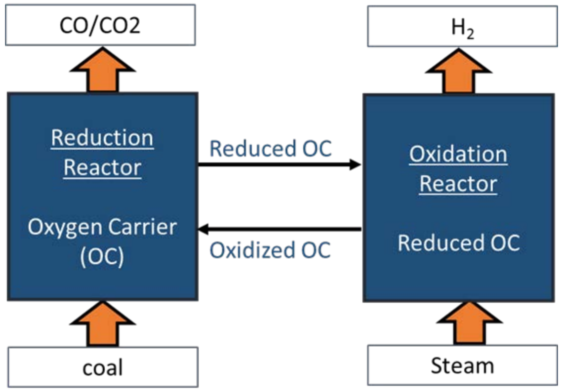
Advantages of NETL Process

Current Commercial Coal Gasification to Produce H2



- ➢Coal + O2 –Air Separation Unit (ASU) required → CO + H2
- ➢CO + H2O → H2 + CO2 – Water gas shift (WGS) reactor required
- ➢Pressure swing adsorption (PSA) used for separation of H2 and CO2 – Added separation cost
- ➢Temperatures are above 1100 C

NETL Process



Advantages of the NETL process

- Oxygen supplied by oxygen carrier -Air separation unit not required – cost reduction
- Pure H2 is produced in the oxidizer –
  - Water gas shift reactor not required -NETL systems study (DOE/NETL-2008/1307) showed the steam decomposition process is more cost effective than water gas shift reactor
  - PSA for CO2/H2 separation not required –cost reduction
- Temperatures are lower – 750-800 C – cost reduction
- Cost of the oxygen carrier - low – Expected $76 per ton
- Initial MO reduction can be performed directly with coal or methane – A strong reducing gases such as syngas is not required as in iron oxide-steam process

Ferrite Carrier Materials

Research Overview

- **Fuel reactor: Characterization of coal and calcium ferrite reaction**

  $MO + C \rightarrow CO\ (\text{Main}) + CO_2 + M$

  - Identification of phases during various stages of reaction X-Ray diffraction (XRD)

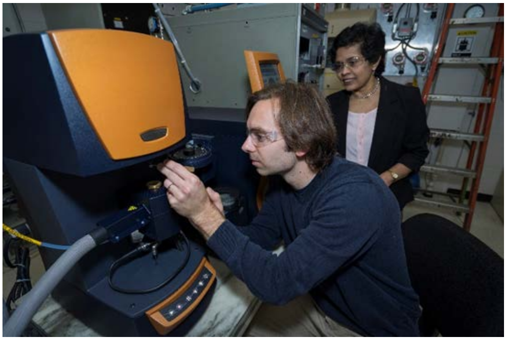
- **Oxidation reactor: Study oxidation of reduced calcium ferrite with steam to produce hydrogen**

  $M + H_2O \rightarrow MO + H_2$

  - Bench scale reactor studies with various coals
  - Kinetic studies
  - Multi cycle tests
  - Tests with a sample from large scale preparation

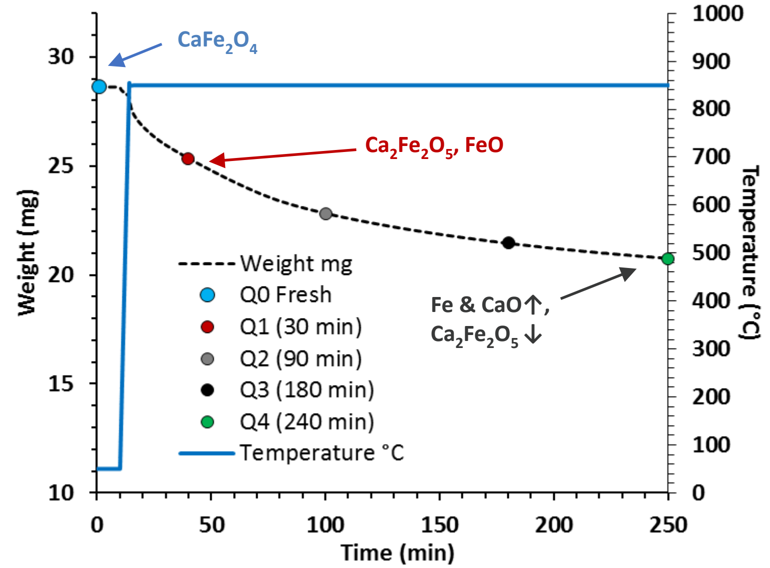
Ferrite Carrier Materials

Fuel Oxidation Studies

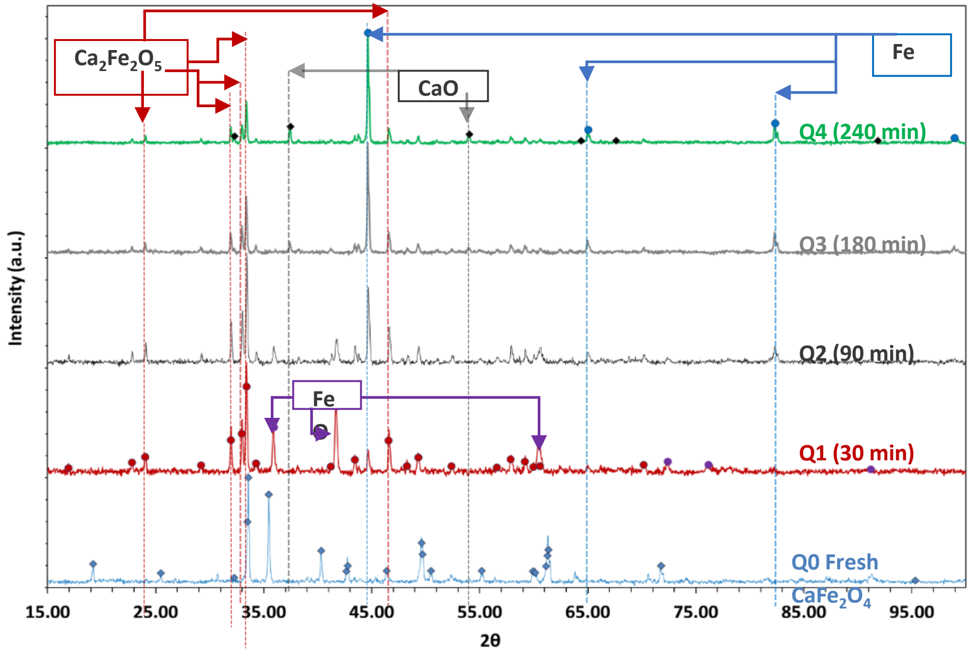


- Wyodak Coal-Ca ferrite mixture placed in TGA
- Rapid ramp T to 850 C
- Samples collected at different times
- XRD Analysis conducted

TGA: Reaction time impact on oxygen release (Controlled reduction sampling)



XRD: Phase reorientation w.r.t. sampling interval



Initial		*Partial Reduction*		*Full Reduction*
$CaFe_2O_4$	$\rightarrow$	$Ca_2Fe_2O_5$ & FeO	$\rightarrow$	CaO & Fe^0

Ferrite Carrier Materials

Research Overview

- **Fuel reactor: Characterization of coal and calcium ferrite reaction**

  $MO + C \rightarrow CO\ (Main) + CO_2 + M$

  - Identification of phases during various stages of reaction X-Ray diffraction (XRD)

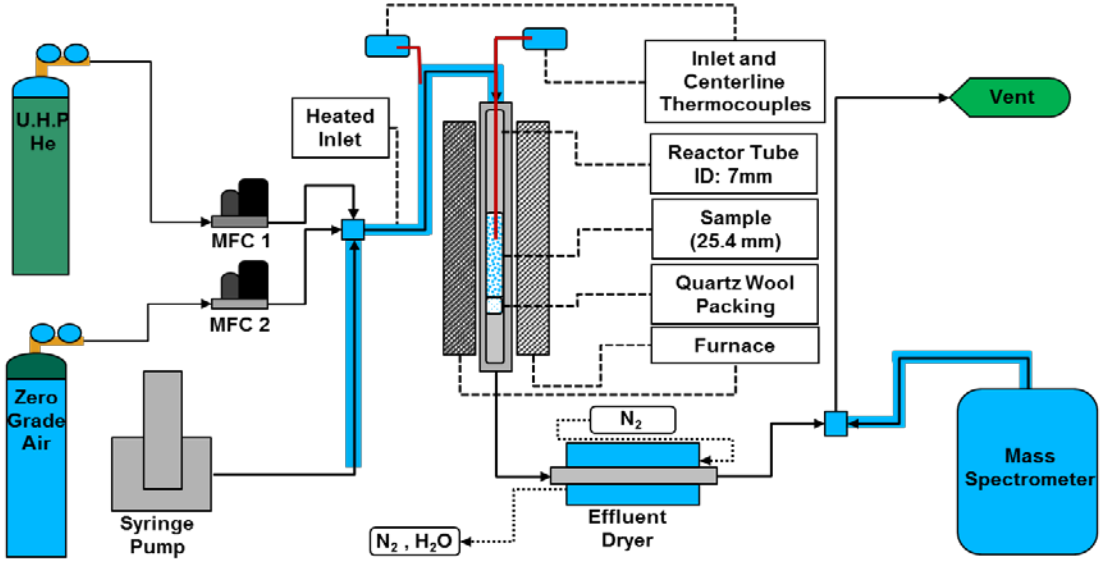
- **Oxidation reactor: Study oxidation of reduced calcium ferrite with steam to produce hydrogen**

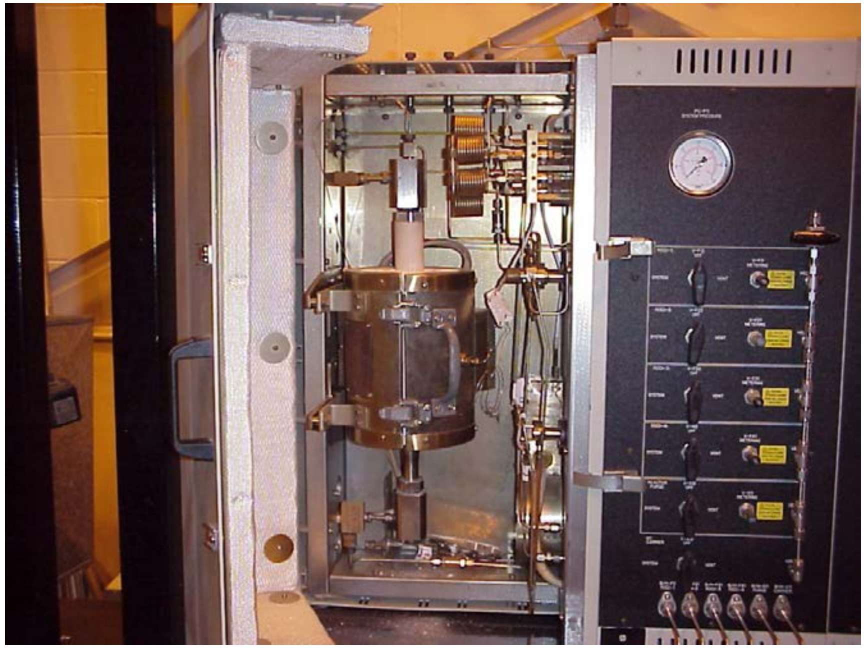
  $M + H_2O \rightarrow MO + H_2$

  - Bench scale reactor studies with various coals
  - Kinetic studies
  - Multi cycle tests
  - Tests with a sample from large scale preparation

Ferrite Carrier Materials

H_2 Production Studies



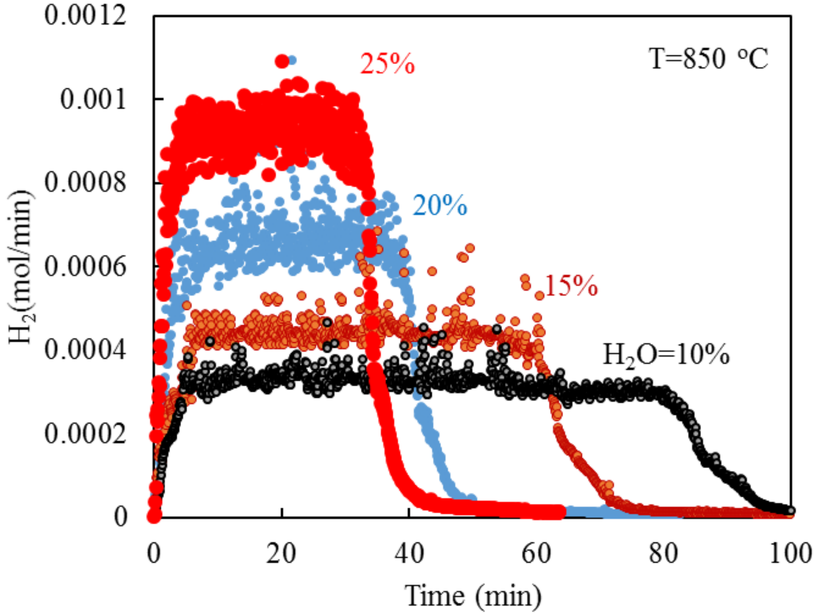


- Coal (0.6 g) mixed with oxygen carrier (4.5 g) placed in the reactor
- Temperature ramp from ambient to 800-850 ^{0}C in Helium at a ramp rate of 4°C/min)& flow rate of 100 cm^3/min (0.1 L/min)
- Isothermal for 60 min.at final T
- When CO level reaches 500 ppm at 800-850 C, 15-25% steam was introduced
- Reactor off gas analyzed by mass spec.

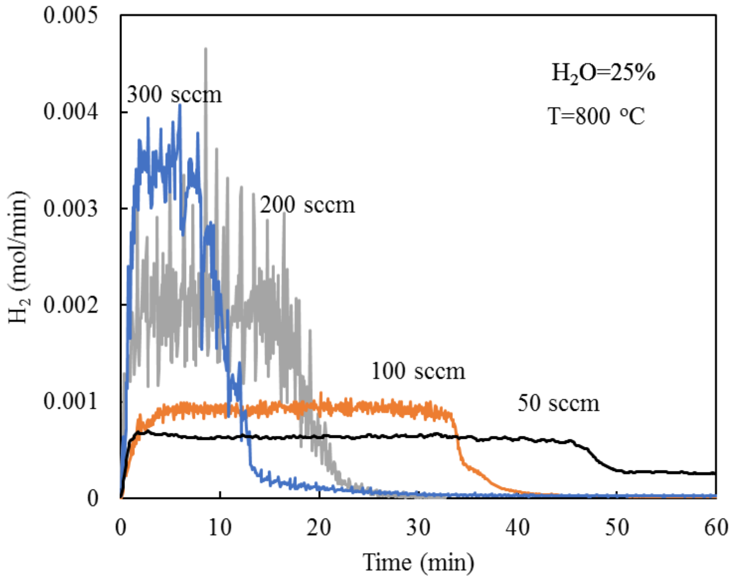
Ferrite Carrier Materials

H_2 Production Studies

Effect of steam concentration (10-25%) on oxidation of reduced $CaFe_2O_4$ at 850 ^oC



Effect of flow rate on oxidation of reduced $CaFe_2O_4$ at 850 ^oC & 25% steam



- Increasing the steam concentration increased H_2 production rates of reduced $CaFe_2O_4$.
- Similar increase in H_2 production rates was observed with increasing flow rate
- Data indicated that the oxidation with steam was very fast

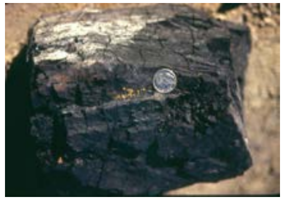
Ferrite Carrier Materials

Evaluation of Coal Types

Table 1a: Proximate and Ultimate Analysis of Coal

		Coal Type				
Analysis	Component (%wt)	Illinois #6 (Bituminous)	Wyodak Coal (Sub Bituminous)	Powder River Basin (PRB) (Sub Bituminous)	Mississippi Lignite	Texas Bottom Seam (Sub Bituminous)
	%Moisture	NA, dry basis	NA, dry basis	NA, dry basis	Na, Dry Basis	Na, Dry Basis
	%Ash	13.39	7.57	8.83	25.71	15.81
	%Vol. Matter	40.83	44.86	40.83	43.76	47.4
	%Fixed Char	45.78	47.57	50.34	30.53	36.79
Ultimate	%Ash	13.39	7.57	8.83	25.71	15.81
	%Carbon	66.05	69.77	67.24	51.75	62.53
	%Hydrogen	4.59	5.65	4.23	3.57	4.74
	%Nitrogen	1.14	0.94	1.53	1.27	1.23
	%Total Sulfur	5.53	0.43	0.38	0.73	0.99
	%Oxygen (diff)	9.3	15.64	17.79	16.97	14.69

Lignite

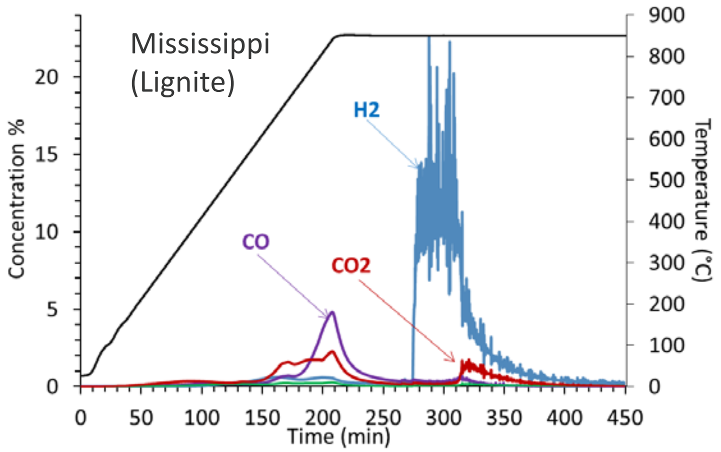


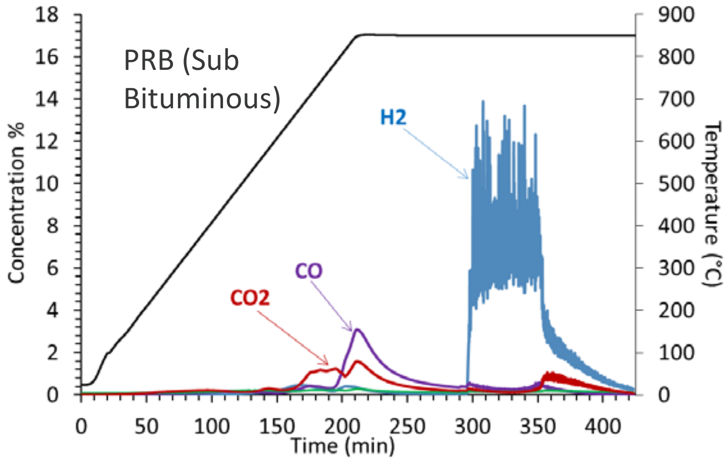
Sub Bituminous

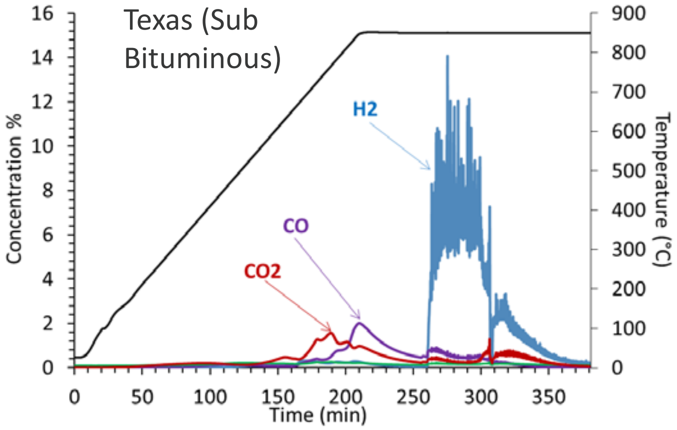
Bituminous

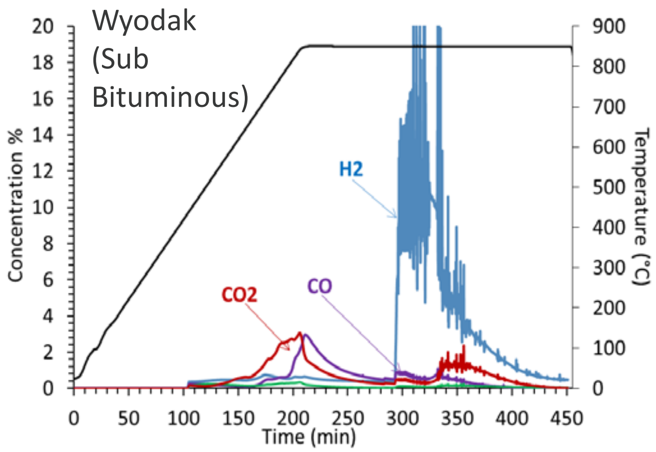
Ferrite Carrier Materials

Coal/Carrier Reactions





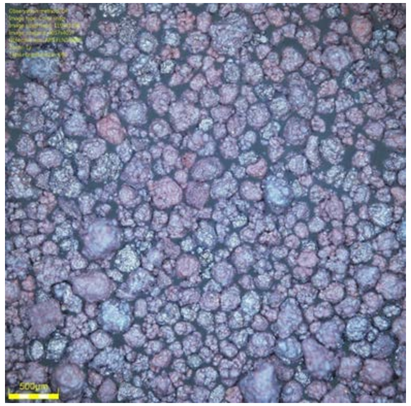




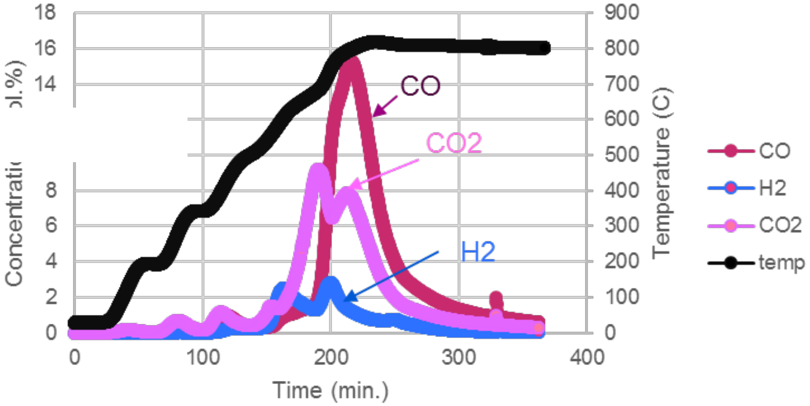
- Reactions were carried out at 850 °C
- All coals reacted with MO to produce CO (main)/CO2
- Reduced M can be oxidized with steam to produce H2
- Conversions as high as ~90% for H2 production observed
- Lignite and sub bituminous coals showed the best reactions
- Conversions with high rank Illinois #6 coal was low

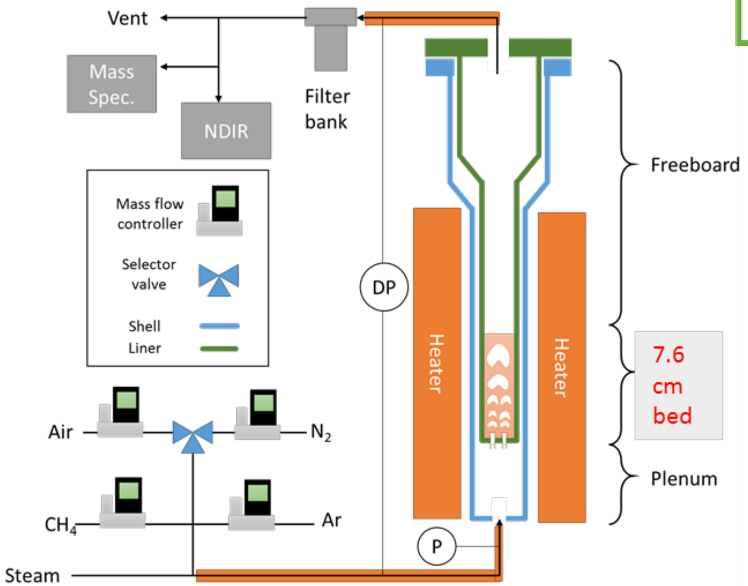
Ferrite Carrier Materials

Scale Up

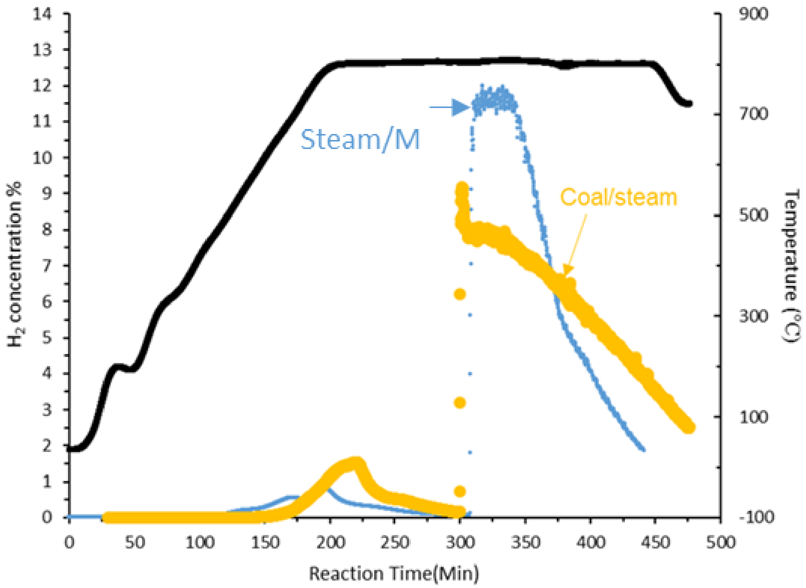


Gas compositions 300g Caferrite-40 g coal without steam





H2 production during steam oxidation at 800 C



- Scale-up production demonstrated
  - 300g Carrier with 40g Wyodak Coal
- H_2 production rate by steam oxidation is higher than that with coal/steam

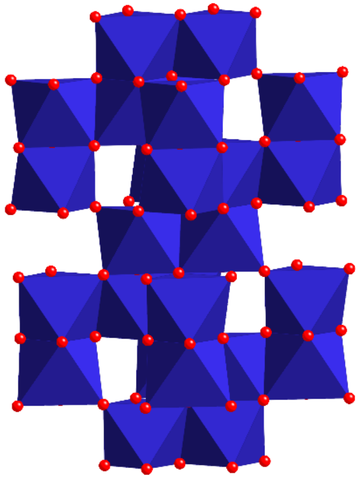
Conclusions

- Sub bituminous and lignite coals react directly with calcium ferrite to form CO(main) and CO_2 (minor)
- Oxidation of reduced oxygen carrier can be performed with steam to produce H_2
- High conversions of H_2 (~80%) was achieved during steam oxidation at 800 °C
- Temperature in the range of 750-850 °C did not have any effect on the rate of steam oxidation
- Steam oxidation rate was highly dependent on the concentration of the steam
- 25-cycle test with oxygen carrier reduction with coal and oxidation with steam showed very stable performance
- Tests with oxygen carrier produced in larger scale has shown promising results

Oxygen Carrier Studies

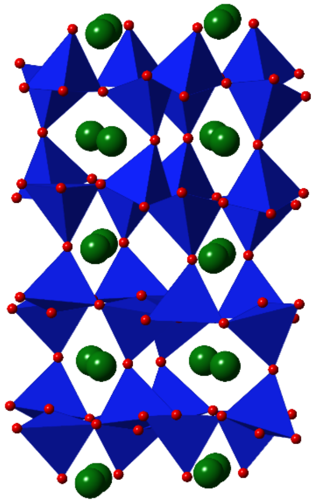
Materials of Interest

Binary Oxides



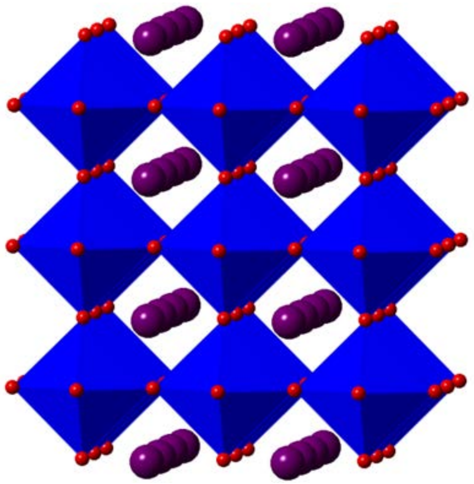
- Inexpensive
- Can have good reactivity
- Limited operating temperature range
- Potential agglomeration

Ferrites



- Can be used for partial oxidation
- Ideal for gasification
- Compositional flexibility
- Stable

Perovskites



- Easily reduced/oxidized
- Compositional flexibility
- Tuneable oxygen capacity and temperature range
- Stable

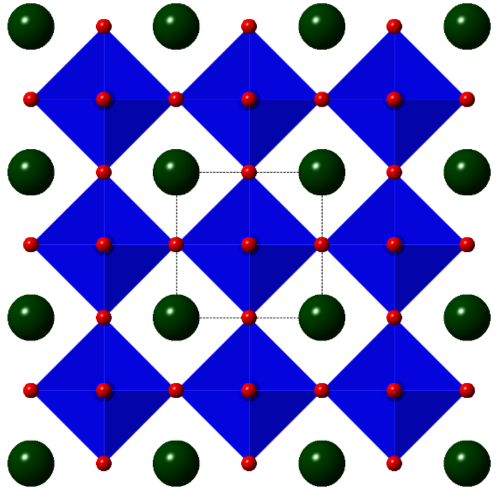
Perovskite Materials

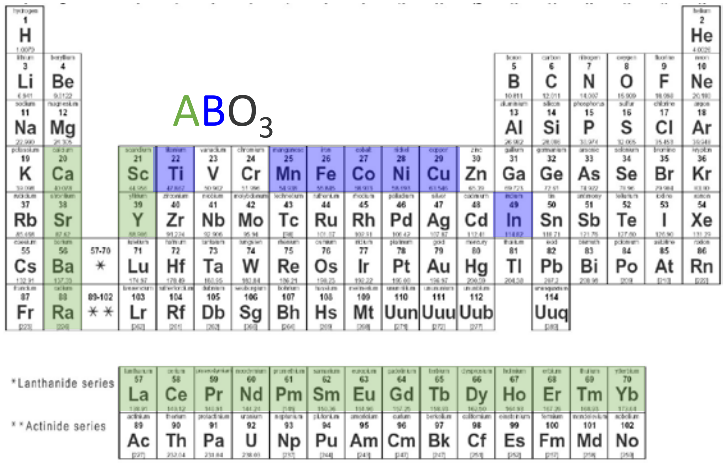
Background

- Perovskites are a well studied type of oxide with the general formula ABO_3
- The first identified Perovskite was $CaTiO_3$
- A-site cation has a dodecahedral coordination
- B-site cation sits in the center of BO_6 octahedra
- "Ideal" structure is cubic though the size of the A-site cation can create distortions

- Applications
  - Chemical looping combustion
    - Potential CLOU candidates, if oxygen is released into the gas phase
  - Pollution remediation
    - NO_x decomposition
  - Replacement of noble metal catalysts in automobiles
  - Syngas production via reforming reactions
  - High Temperature Gas Sensors
  - Solid Oxide Fuel Cells
  - Photovoltaics

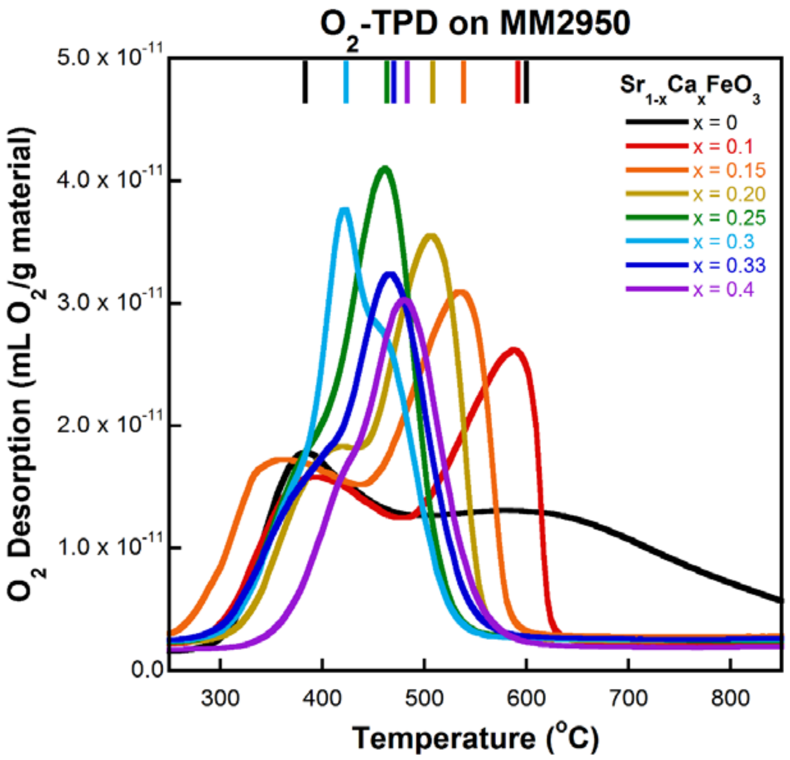
- Potentially Interesting Properties
  - Superconductivity
  - Magnetoresistance
  - Ferromagnetism



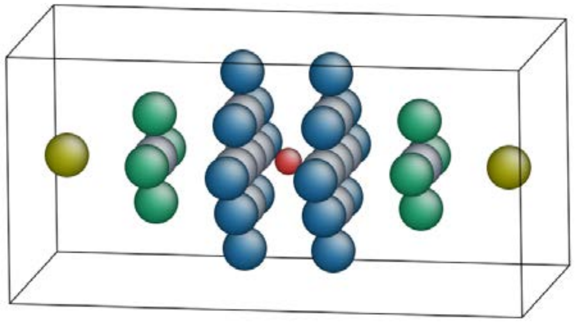


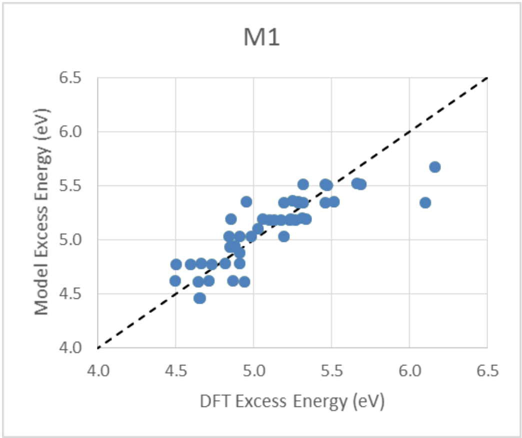
Oxygen Carrier Studies

Tuning Oxygen Desorption in Perovskites



- Low-to-Moderate doping (x = 0 – 0.3)
  - Systematic decrease in O_2 desorption temperature
- Larger Ca^{2+} doping (x = 0.3 – 0.4)
  - Systematic increase in O_2 desorption temperature





- **Collaboration with CMU and IDAES**
  - Dominic Alfonso (NETL)
  - De Nyago Tafen (NETL)
  - David Miller (NETL)
  - Christopher Hanselman (CMU)
  - Chrysanthos Gounaris (CMU)
- **Using computational tools to investigate substitutional motifs in perovskite materials**

IDAES Institute for the Design of Advanced Energy Systems

CARNEGIE MELLON UNIVERSITY PITTSBURGH PENNSYLVANIA 1900

Acknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

- **Experimental**
  - Sittichai Natesakhawat
  - Yunyun Zhou
  - Elliot Roth
  - Douglas Kauffman
  - Christopher Matranga
- **Computational**
  - Dominic Alfonso
  - De Nyago Tafen
  - David Miller
- **Collaborators**
  - Chrysanthos Gounaris
  - Christopher Hanselman
  - Jun-sik Lee

IDAES Institute for the Design of Advanced Energy Systems

CAMD

BROOKHAVEN NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

CARNEGIE MELLON UNIVERSITY PITTSBURGH PENNSYLVANIA 1900

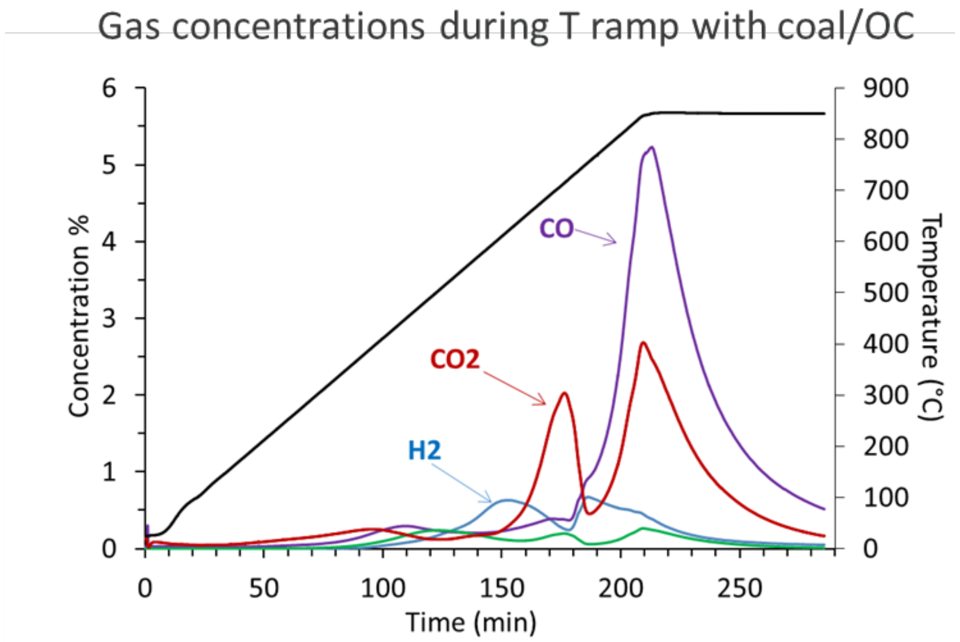
Argonne NATIONAL LABORATORY

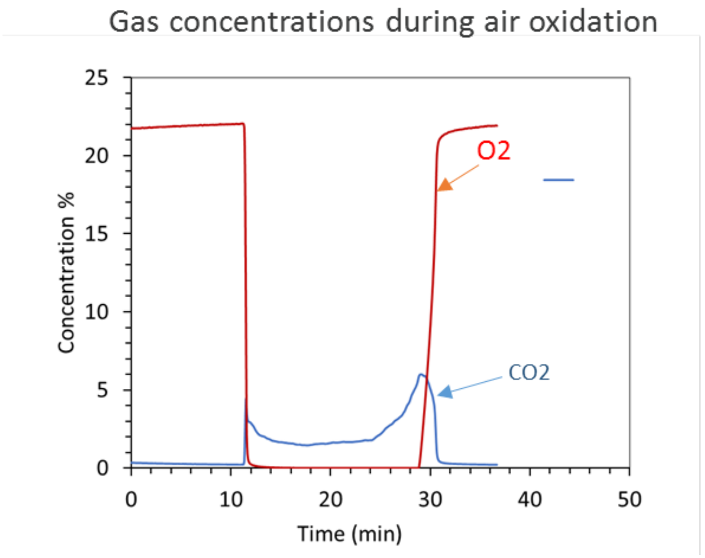
- **DISCLAIMER**
  - This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with AECOM. Neither the United States Government nor any agency thereof, nor any of their employees, nor AECOM, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

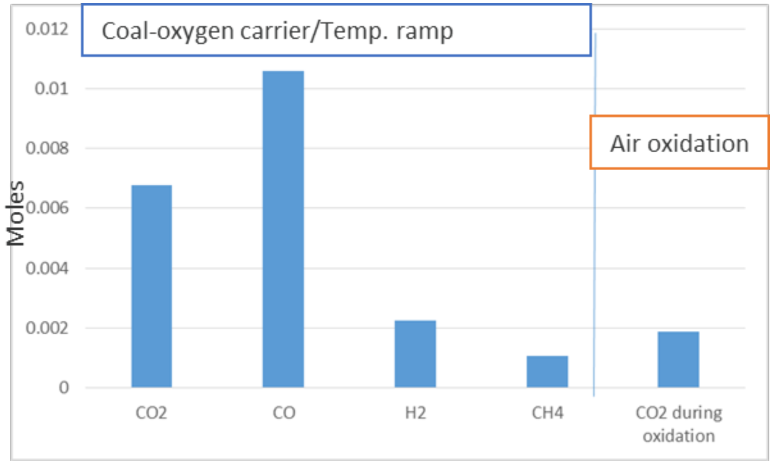
Questions?

Investigation of optimum coal to oxygen carrier (OC) ratio

Gas compositions during the temperature ramp of Wyodak coal (0.6)/calcium ferrite(4.5 g) in Helium and during oxidation with air at 850 C



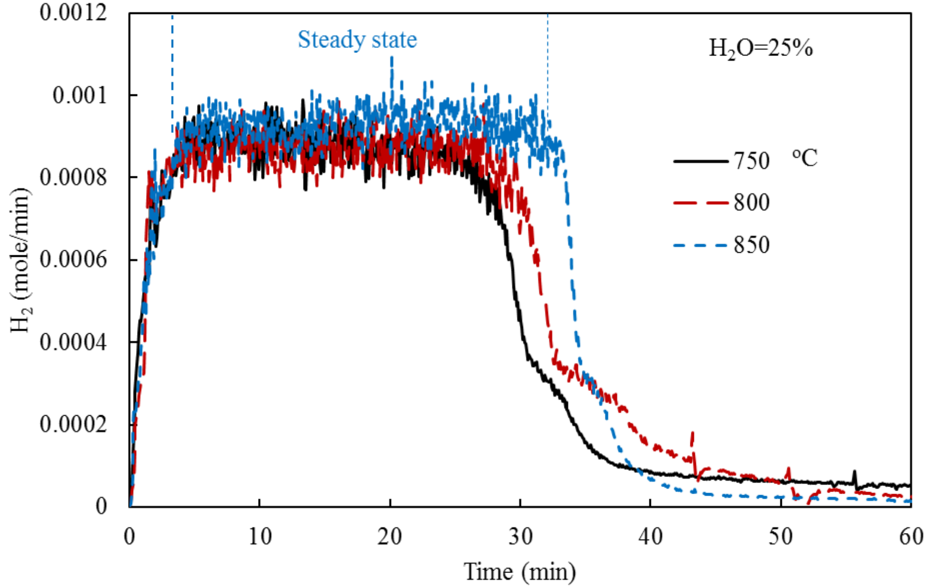




- Coal to OC ratio was varied to obtain full utilization of coal due to reaction with OC during the temperature ramp
- 4.5 g of oxygen carrier to 0.6g coal was the best
- CO (main)/CO2(minor) was observed during temperature ramp with oxygen carrier
- Coal was fully utilized-minimal CO2 during oxidation
- A small amount of CO2 observed during air oxidation may be due the oxidation of coal remained in the walls of reactor not in contact with OC

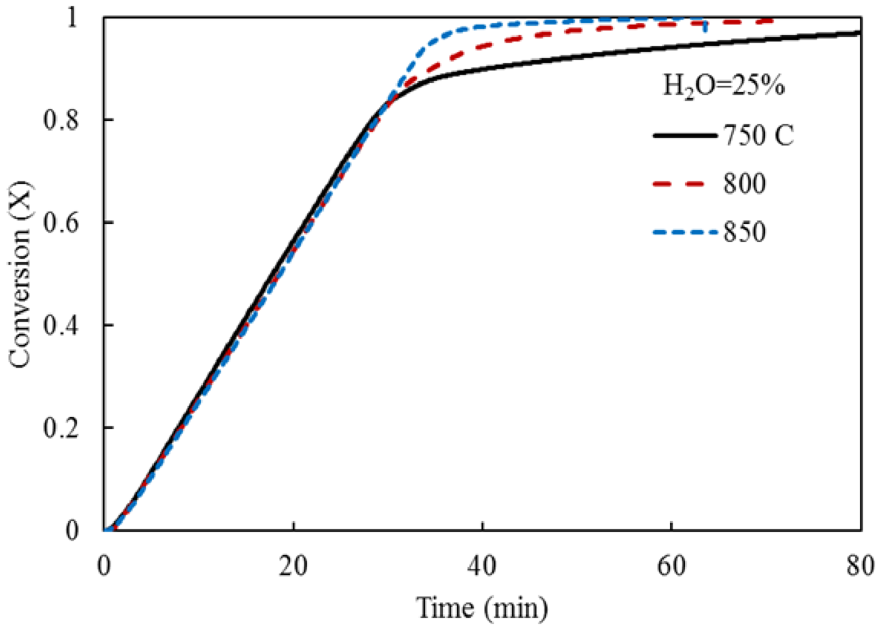
Effect of temperature on H2 production during steam oxidation (MO initially reacted with Wyodak coal)

Oxidation of reduced $CaFe_2O_4$ with 25% steam/He at 750, 800, and 850 °C



- H_2 production reached steady state fast
- Temperature had minimal effect on the initial H_2 production

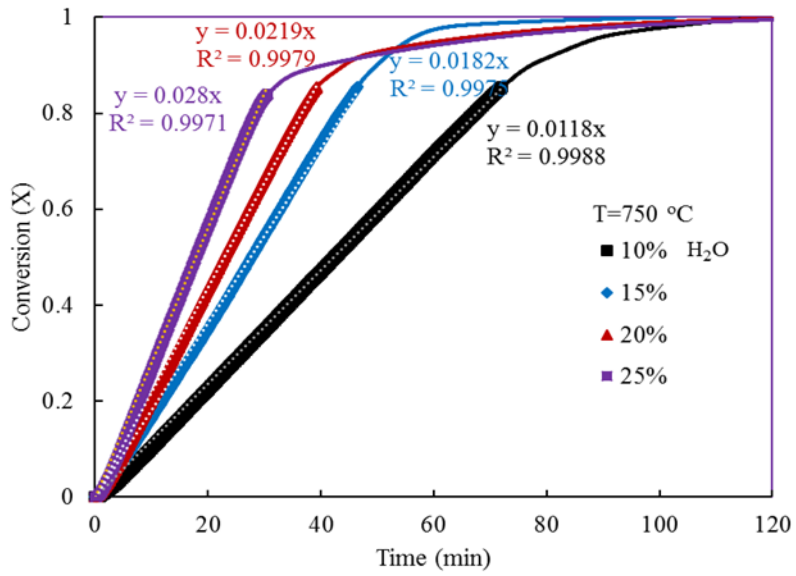
Degree of oxidation conversion (X) of reduced $CaFe_2O_4$ at 750, 800, and 850 °C with 25% steam.

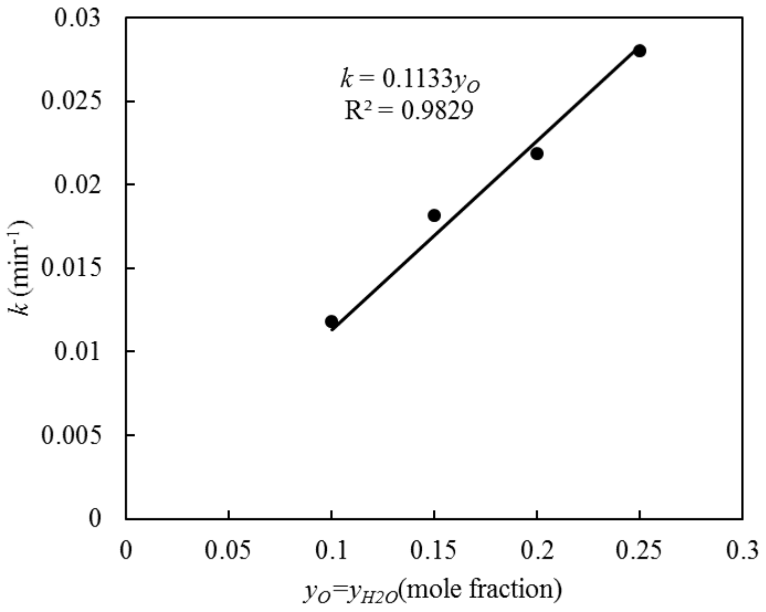


- Conversion rate had minimal effect on temperature up to 80% conversion
- Final conversion was only slightly higher at higher temperature

Rate Analysis

The extent of oxidation with different steam concentrations (10, 15, 20, and 25%) at 750 ^{o}C.



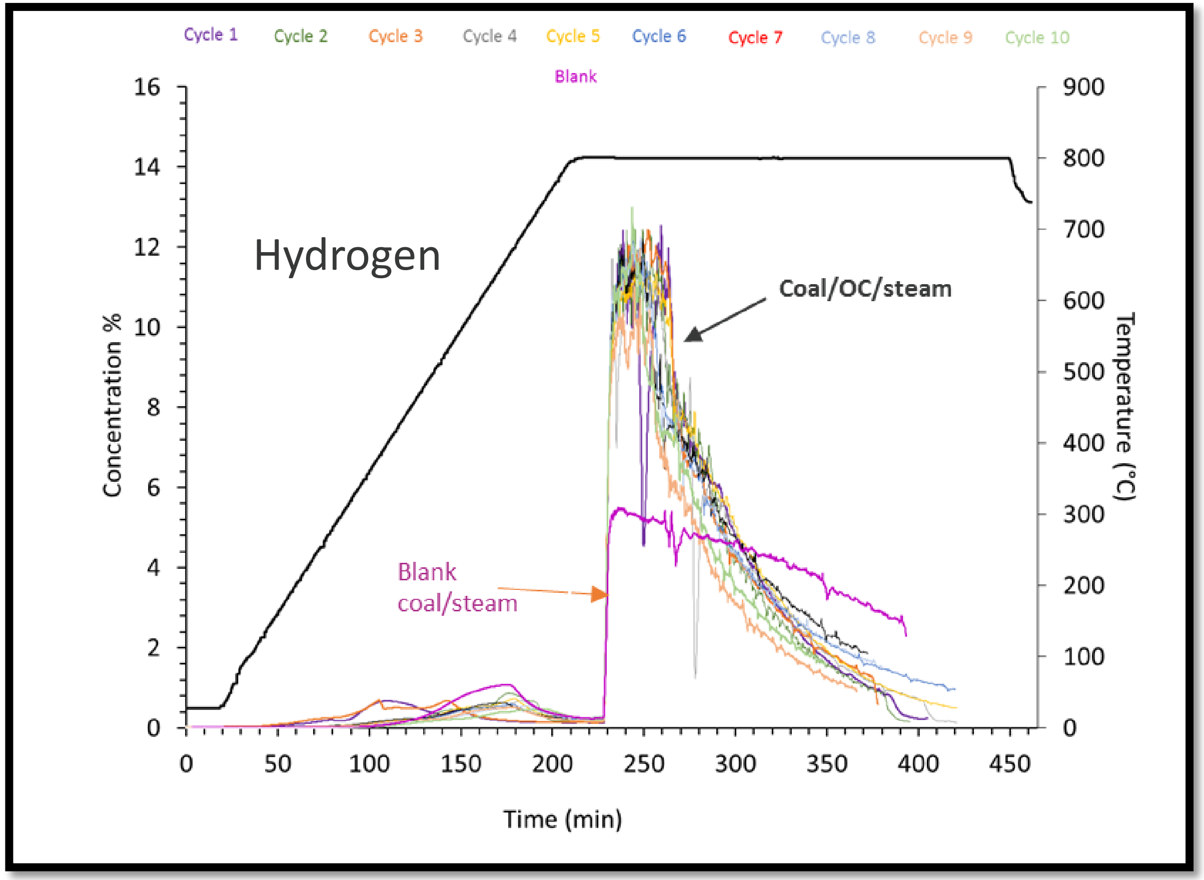


- The uptake rates were analyzed by plotting conversion (X) as a function of time, which resulted in a straight line indicating a linear rate
- A wide variety of rate laws were used to fit the conversion (X)-time (t) data
- The outcomes implied that the oxygen uptake can be best explained by a zero-order rate model
- Rate parameters related to oxidation were obtained from this model

H2 production data during cycle tests with Coal/MO/steam

(Temperature ramp from ambient to 800 C, 15% steam at 800 C)

Hydrogen during Wyodak-15% steam 10 cycle

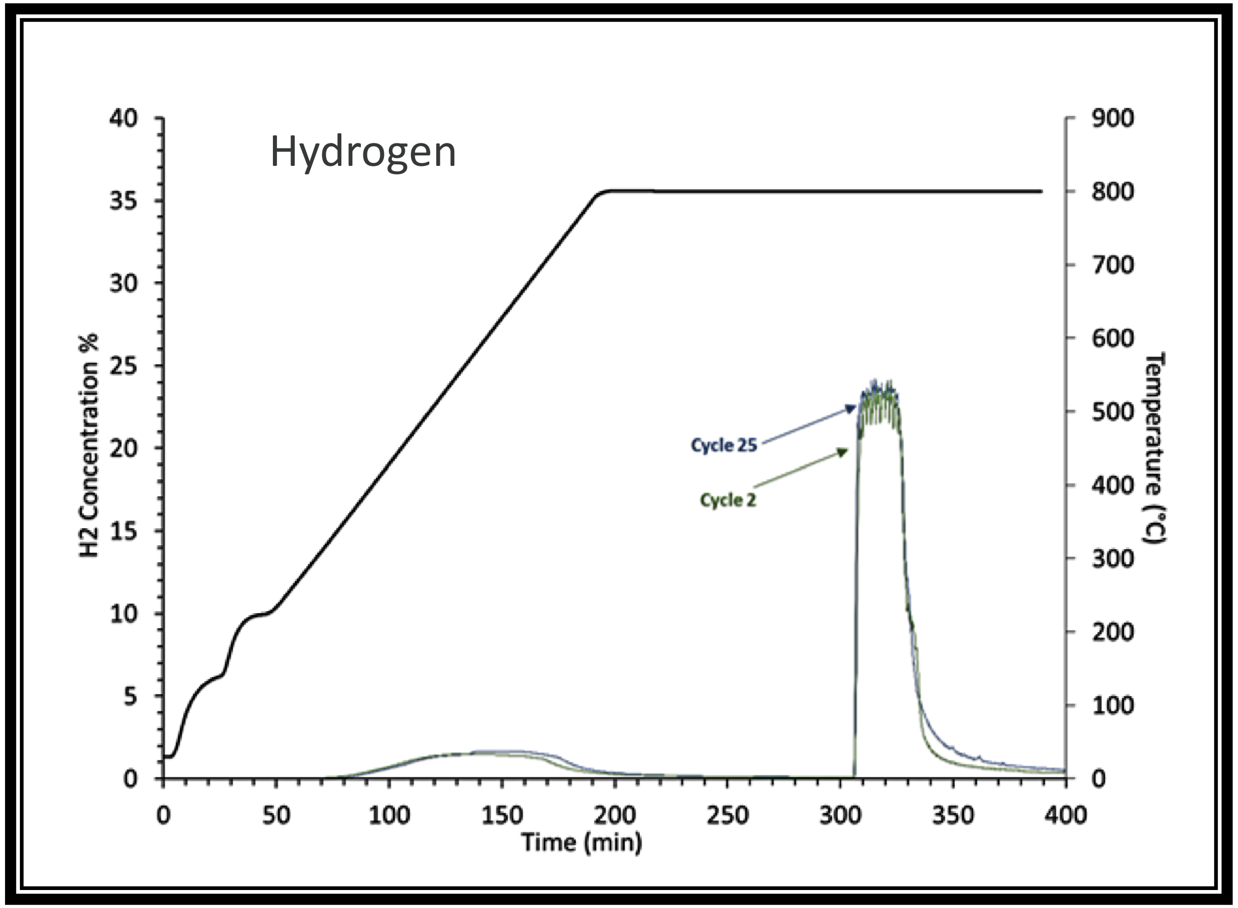


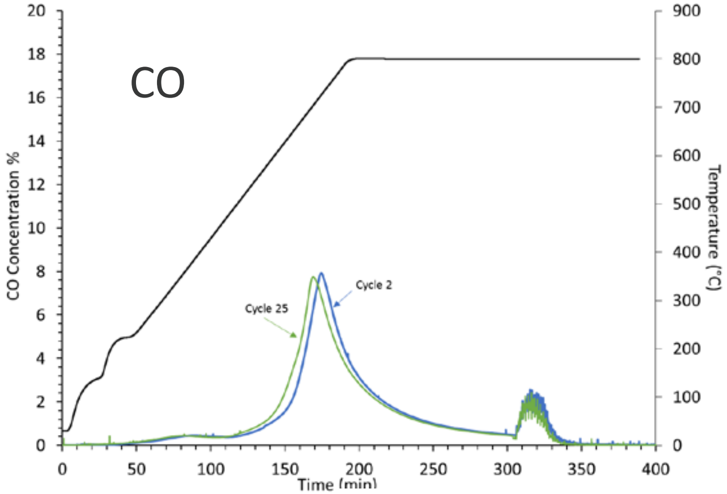
Experimental

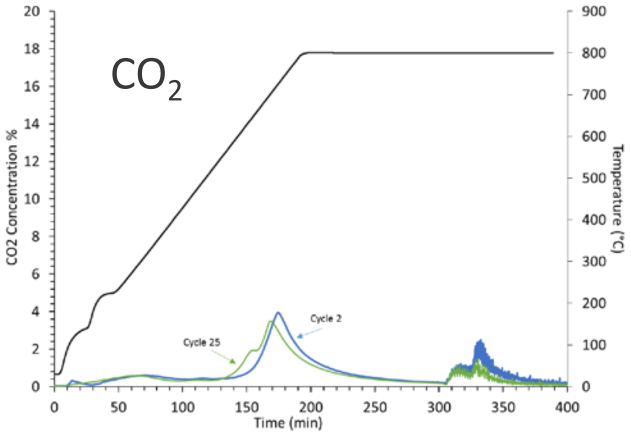
- Mix MO:coal (4.5 g :0.6 g (Wyodak) or 9g:1.2g (Lignite))
- Ramp T from ambient to 800 ^{0}C
- Introduce 15-25% steam at 800 ^{0}C
- Cool Back to ambient & remove MO
- Mix MO with new coal Repeat T ramp/steam in the next cycle

- H_2 production rates significantly better with MO/Coal/steam than that with coal/steam blank
- Stable production of H_2 during the cyclic tests despite possible MO loss during transfer
- 80% steam conversion to H2

Lignite coal – 25% steam 25 cycle

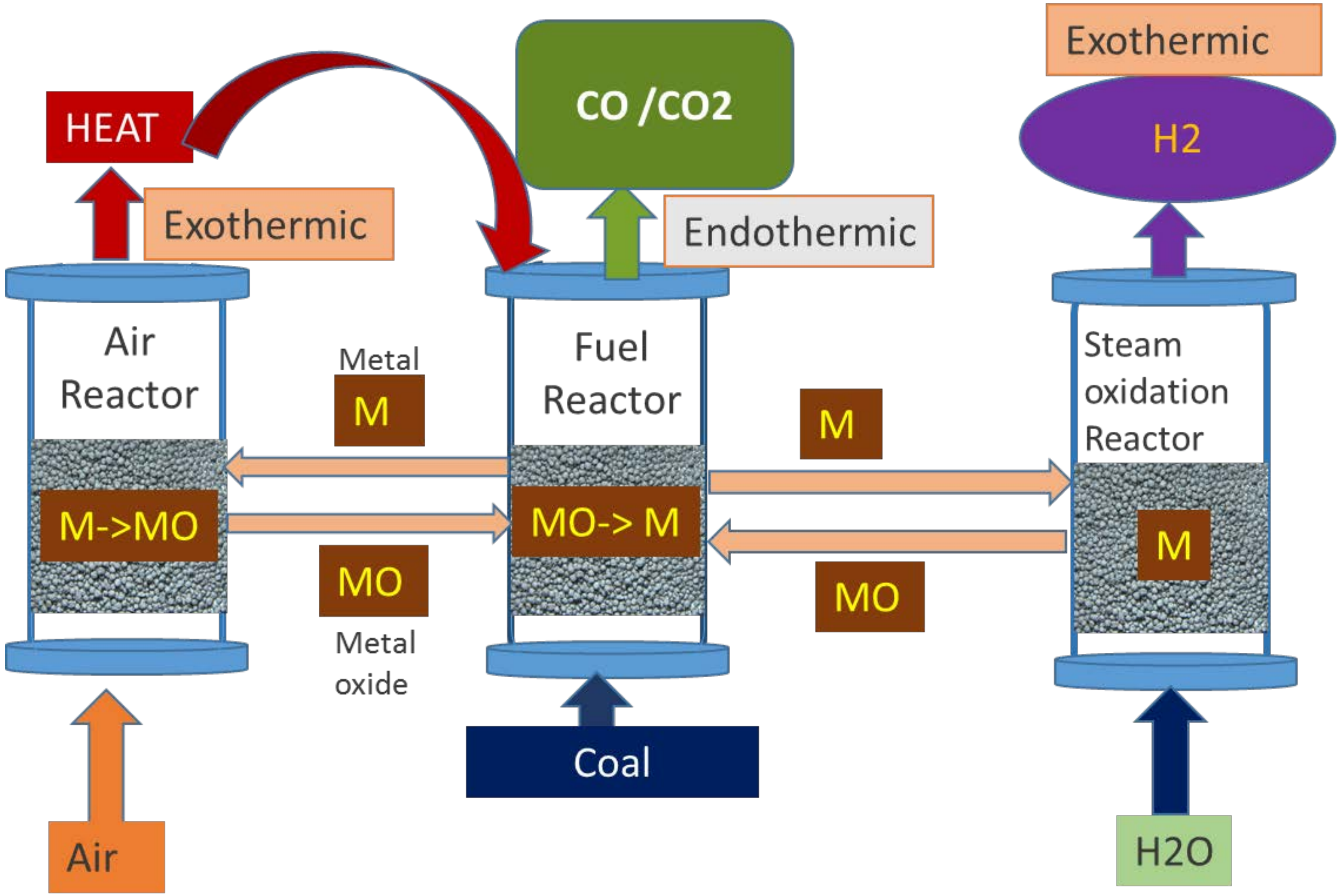






- Stable performance was observed with lignite coal during 25 cycles

Heat requirements



- Overall process is endothermic
- Estimated endothermic heat for fuel reactor is 558 KJ/mole of MO
- Estimated exothermic heat for steam oxidation reactor is 174 KJ/mole of MO
- Heat can be provided by M oxidation with air if CO_2 emission is a consideration