Pilot Scale Testing of the Carbon Negative, Product-Flexible Syngas Chemical Looping Process

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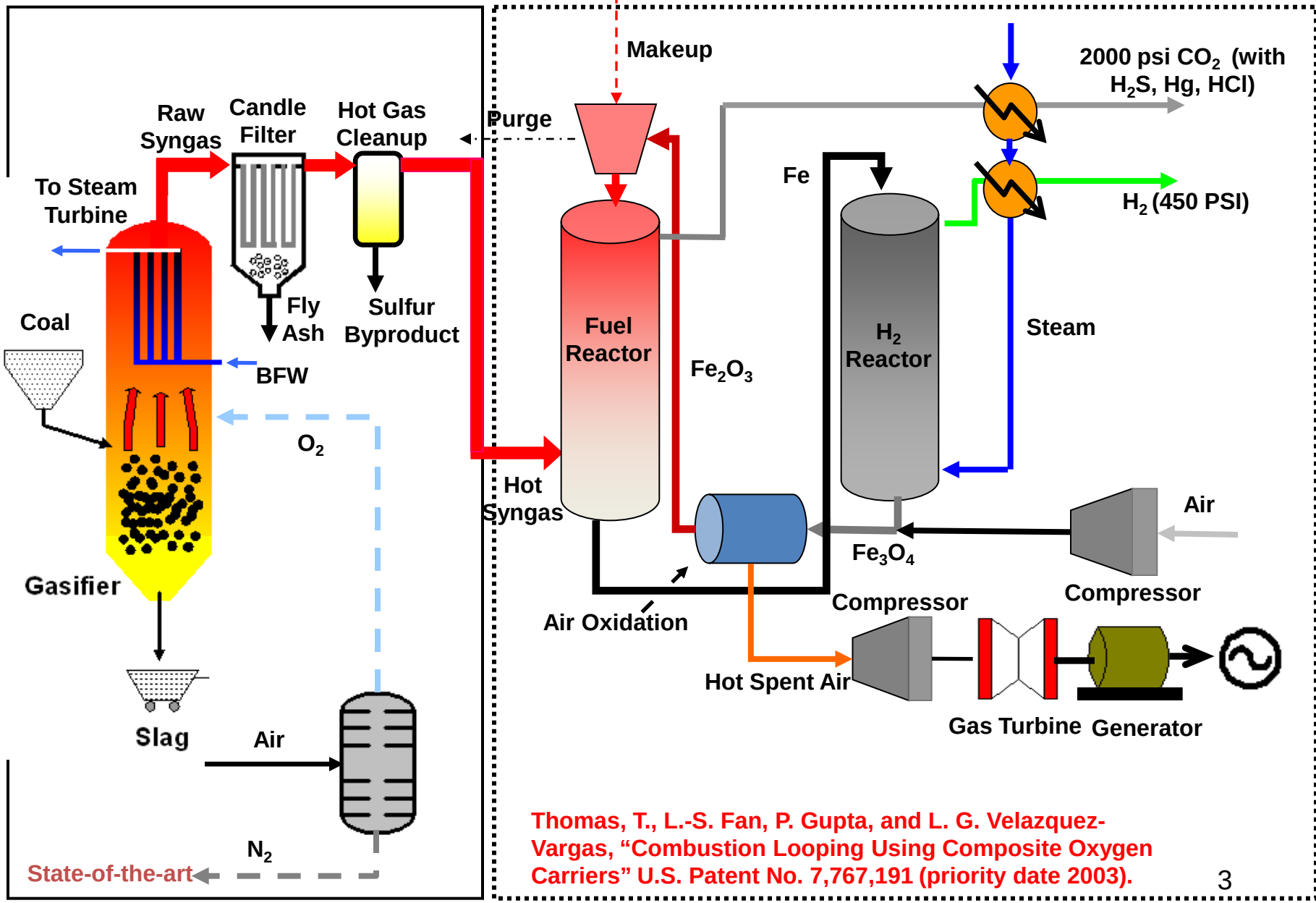
Pilot Scale Testing of the Carbon Negative, Product-flexible Syngas Chemical Looping Process

- **Novelty and Readiness of the Proposed Technology**
  - 10 – 20% improvement for power generation, hydrogen production, and liquid fuel synthesis with nearly 100% CO_2 capture
  - Successful bench and sub-pilot scale demonstrations
- **Project Objectives**
  - Pilot unit design and construction at NCCC
  - Long term continuous operation
  - Validate the techno-economic attractiveness of SCL
- **Potential Impacts**
  - GHG Emission Reduction
  - Energy Efficiency Enhancement
  - Energy Security Improvement
- **Budget**
  - $5 million from DOE ARPA-E
  - $4.9355 million cost share

OSU Syngas Chemical Looping Process



Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (priority date 2003).

Key Project Tasks

1. Oxygen Carrier Particle Optimization and Preparation
2. Sub-Pilot Unit Operation and Data Crosschecking
3. Full Size Cold Model Design, Construction and Operation
4. Pilot Plant Design and Cost Estimate
5. Pilot Plant Construction, Shakedown, and Operation
6. Techno-Economic Analysis and Commercialization Plan

Status of the Key Tasks

1. **Oxygen Carrier Particle Optimization and Preparation (OSU)**
   - Hundreds of formulas have been tested
   - Quantum mechanism study assisting formula development
   - Tested in both bench scale and subpilot scale unit demonstration
   - > 99.5% Pure CO_2 and >99.95% Pure Hydrogen Obtained
   - Particle reactivity and strength maintained after cycles

Oxygen Carrier Development

Desired Properties

- Good oxygen carrying capacity
- Good reducer/oxidizer gas conversions
- High rates of reaction
- Satisfactory long term recyclability and durability
- Good Mechanical Strength
- Suitable heat capacity and high melting points
- Low cost and ease in scale up of synthesis procedure
- Resistance to contaminant
- inhibition of carbon formations
- Health and Environmental Impacts

Possible Oxygen Carrier Candidates

- Nickel Oxide
- Copper Oxide
- Iron Oxide
- Cobalt Oxide

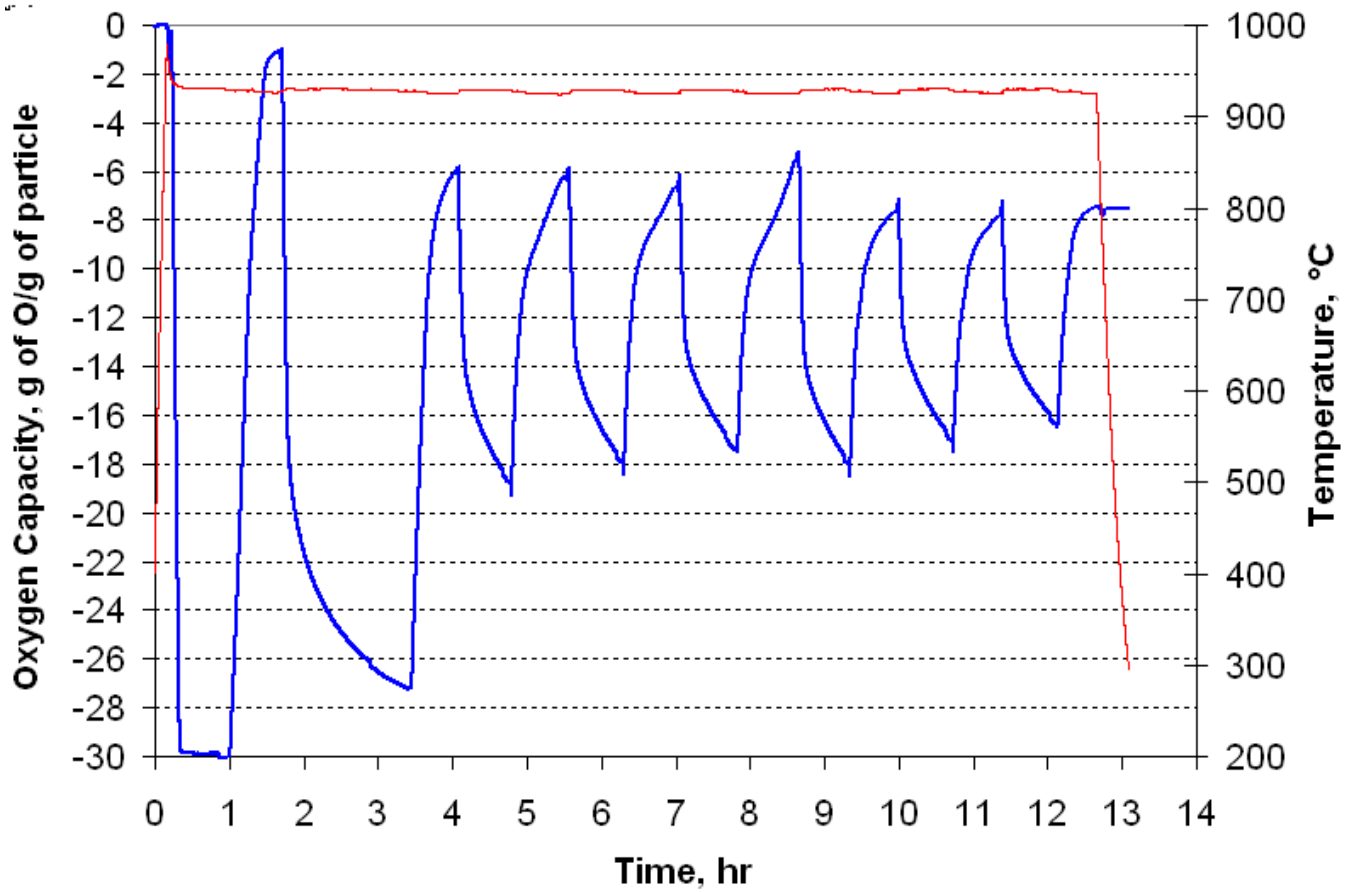
Key Property Comparisons of Potential Metal Oxide Candidates

	Fe_2O_3	NiO	CuO	CoO
Cost	+	–	~	–
Oxygen Capacity (wt %)	30	21	20	21
Thermodynamics	+	+	+	+
Kinetics/Reactivity	–	+	+	–
Melting Points	+	~	–	+
Strength	+	–	~	~
Environmental& Health	~	–	~	–

+: positive; –: negative; ~neutral

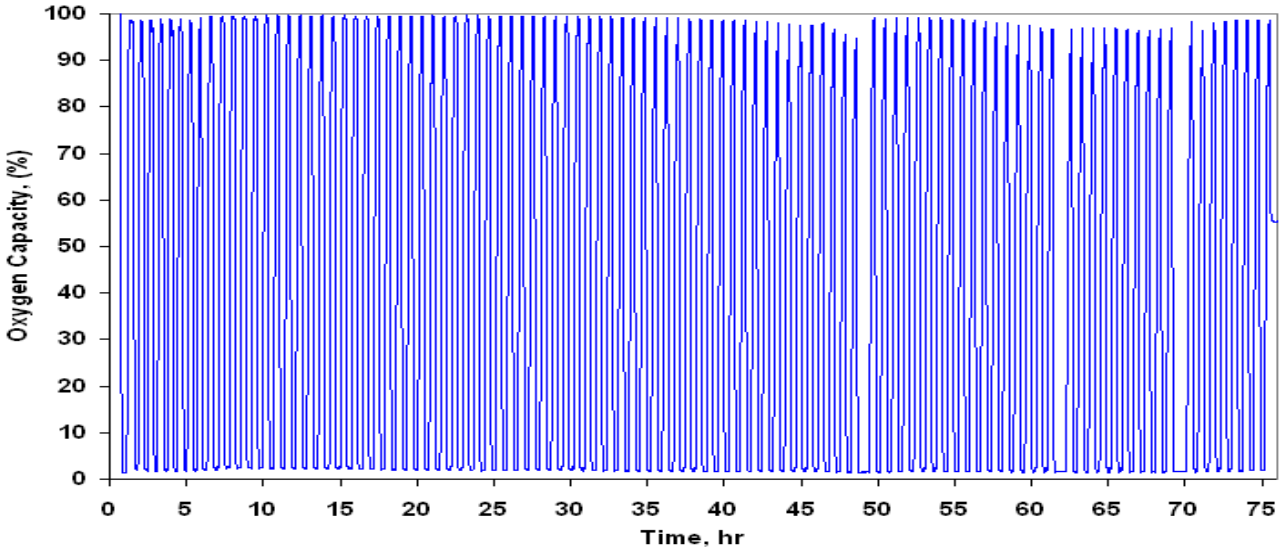
Some Tested Supported Metal Oxide Vials

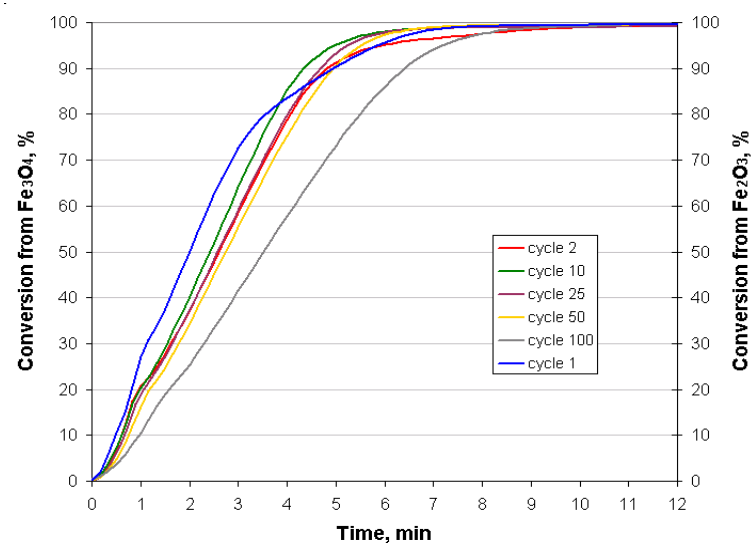
Recyclability of Commercial Fe_2O_3



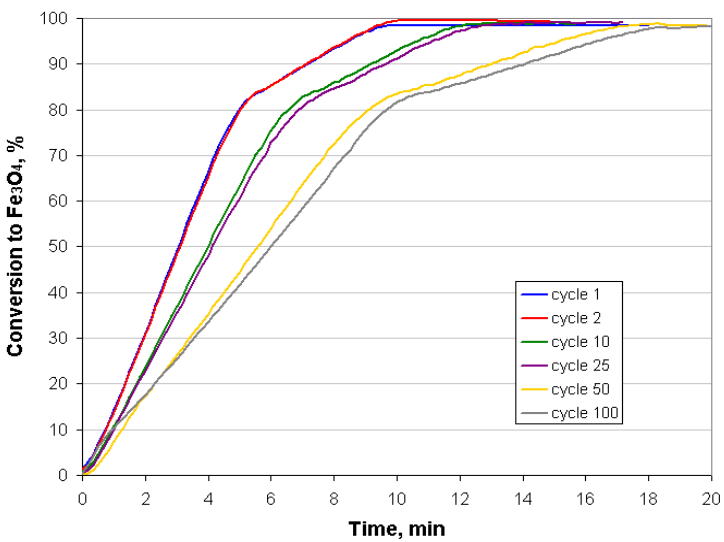
Pure Fe_2O_3 loses its reactivity within the first few redox cycles

Recyclability of Composite Fe_2O_3 Particles





Reduction



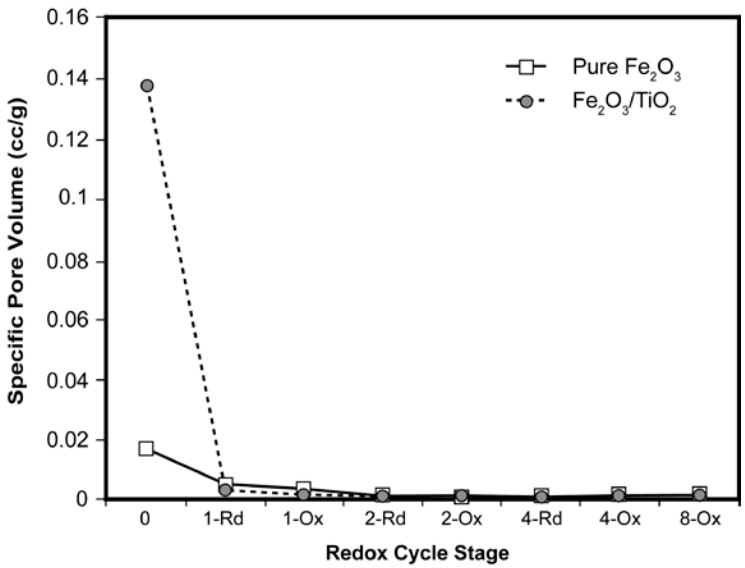
Oxidation

Iron Based Composite particles are completely recyclable for more than 100 cycles

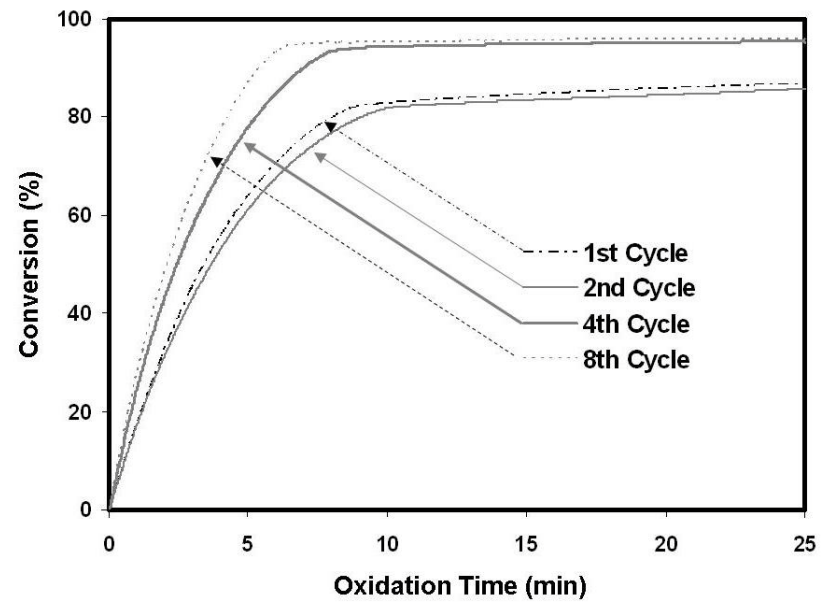
Role of Support – Preliminary Experiment

Conventional Opinion: Support addition increases pore volume, surface area, and sintering resistance of the oxygen carrier

Experimental Results:



Pore volume of both pure and supported iron oxide decrease significantly with redox cycles

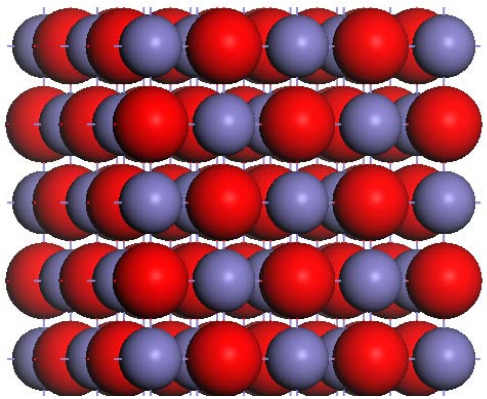


Reactivity of supported iron oxide increases with decreasing pore volume

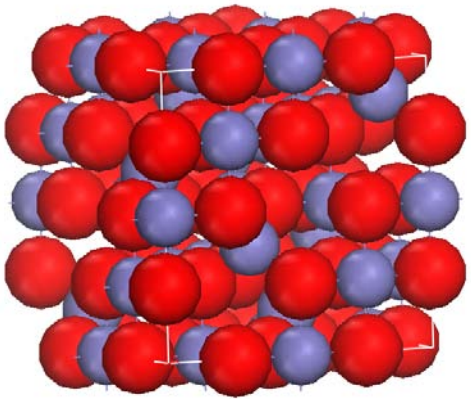
Conventional opinion on the role of support may not be accurate

Structures of Iron Oxide

FeO

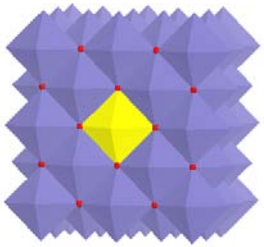


Fe_3O_4



NaCl Type

- oxygen close-packed cubic pattern
- iron occupy all **octahedral** interstices



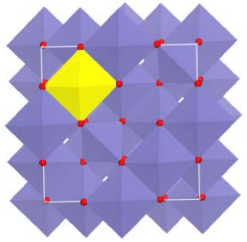
inverse Spinel Type

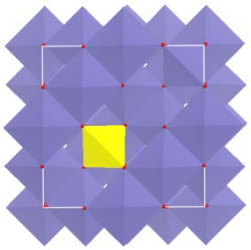
octahedral interstices

1/2 occupation rate

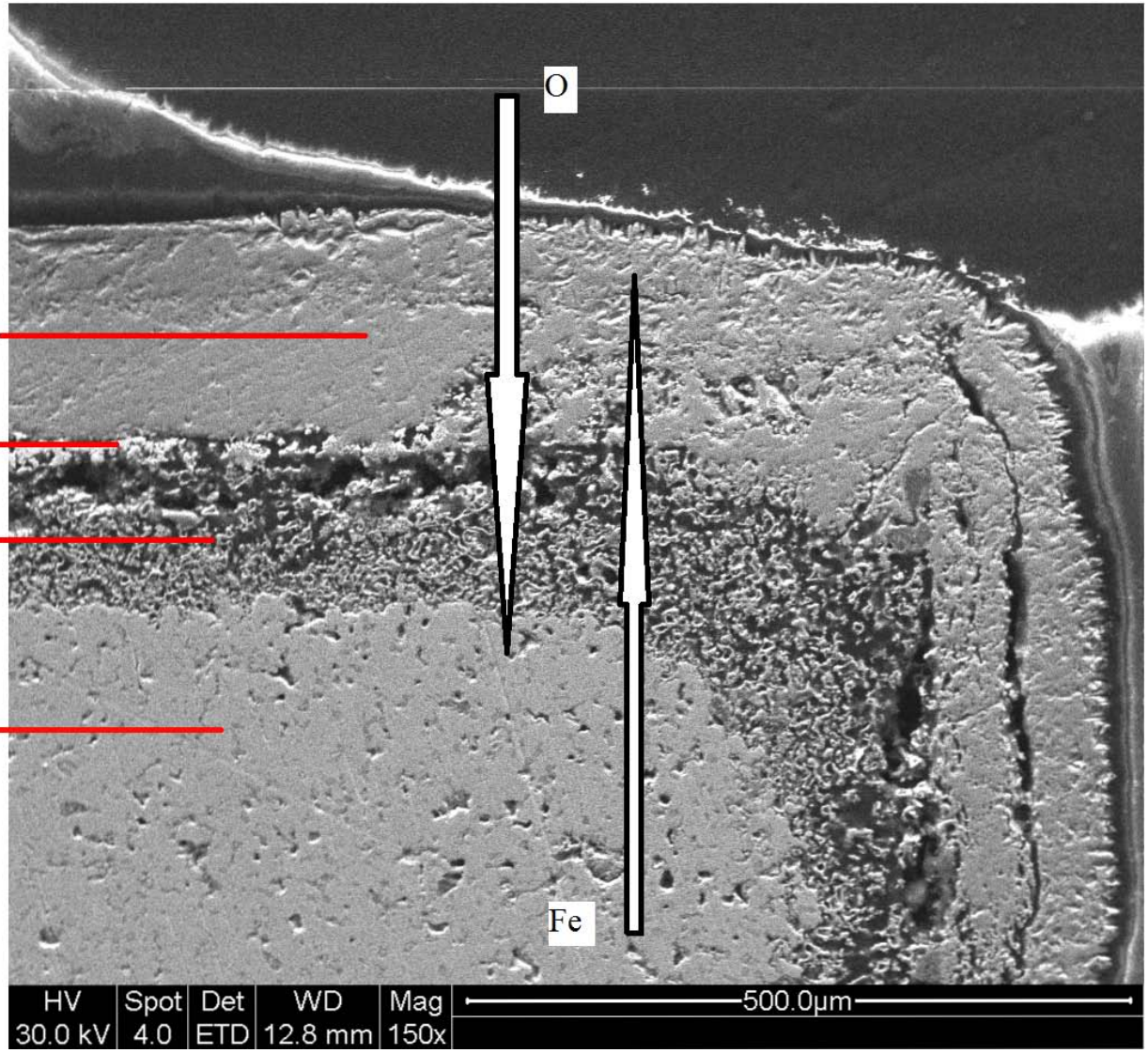
tetrahedral interstices

1/8 occupation rate





Pellet Reaction Mechanism – Ionic Diffusion for Unsupported Iron



Iron Oxide Shell

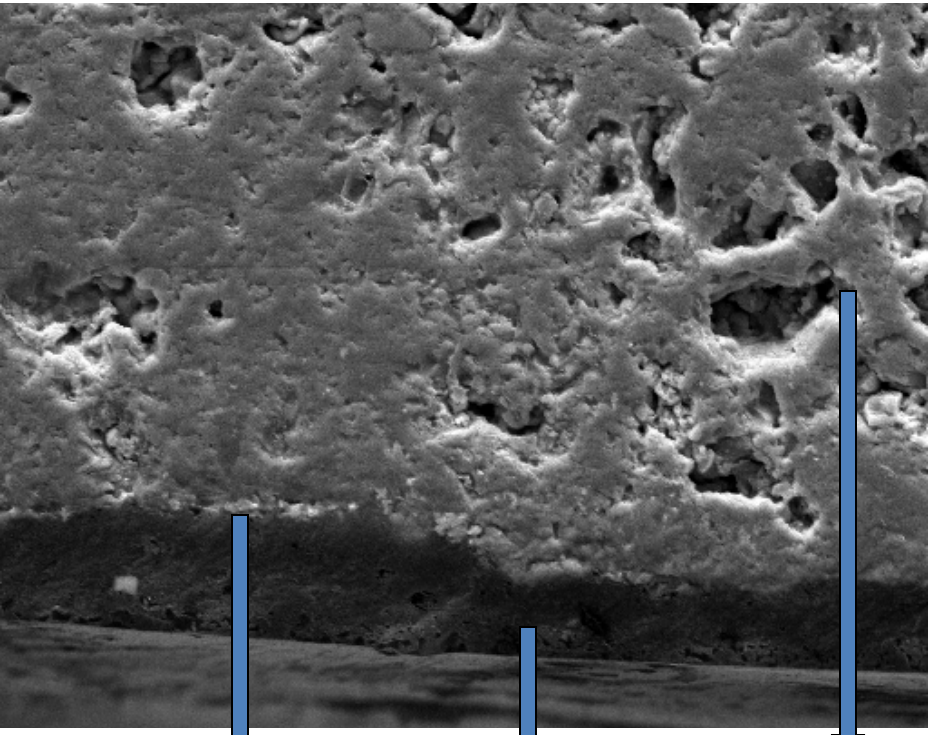
Pt Marker

Iron Oxide Structure

Pure Iron

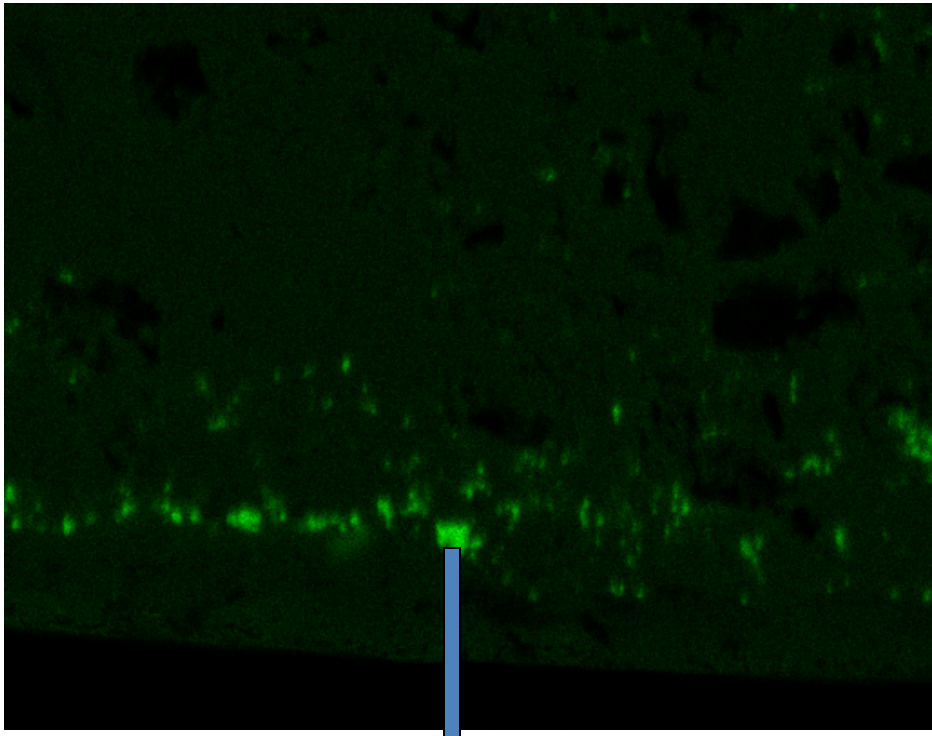
Pellet Reaction Mechanism – Ionic Diffusion for Supported Iron

Partially oxidized Fe with support



Pt Epoxy Resin Pellet bulk phase

Pt mapping

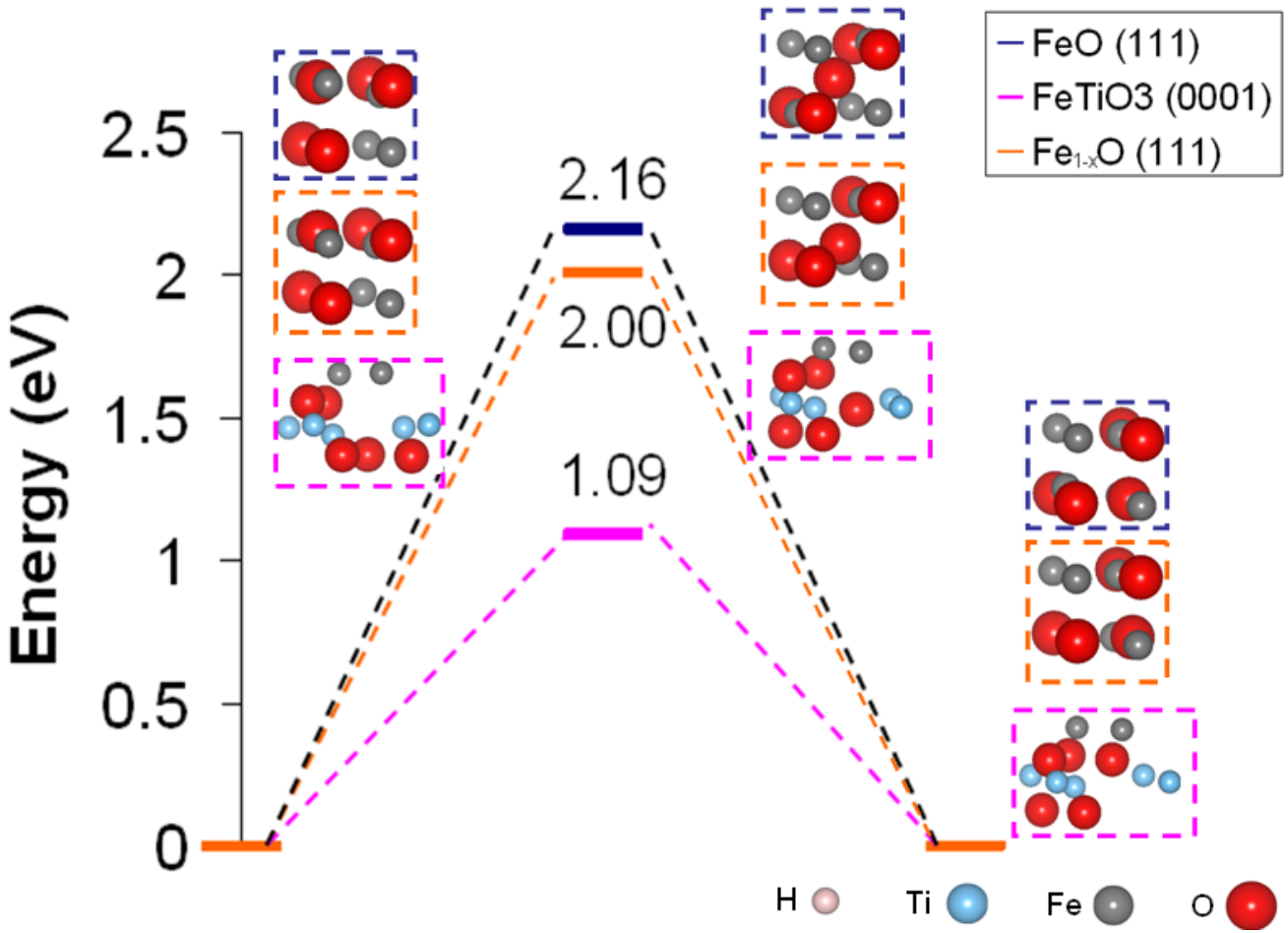


Pt

Role of Support – Oxidation of Fe and Fe/TiO_2

Simulation

Oxygen anion transfer in Wüstite and Ilemnite

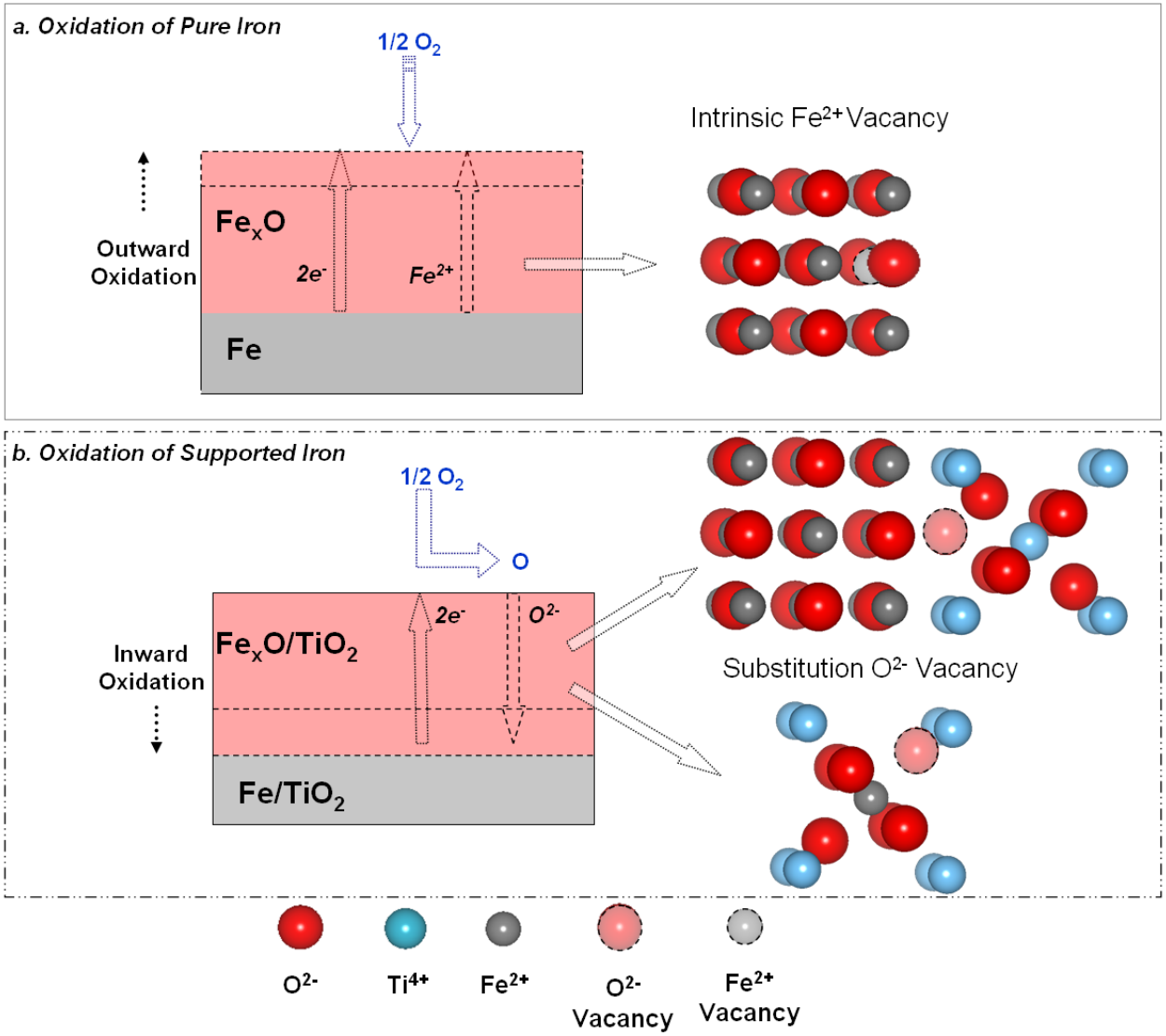


Energy barrier for O^{2-} can be reduced after support addition

Role of Support – Summary

a. For Pure Iron (Oxide): Fe Cations Diffuse via Intrinsic Fe^{x+} Vacancy

b. For Supported Iron (Oxide): O^{2-} Anions Diffuse via O^{2-}Vacancy Created by Support Addition



Oxygen carrier development should focus on the enhancement of the ionic diffusion of oxygen

Status of the Key Tasks (cont.)

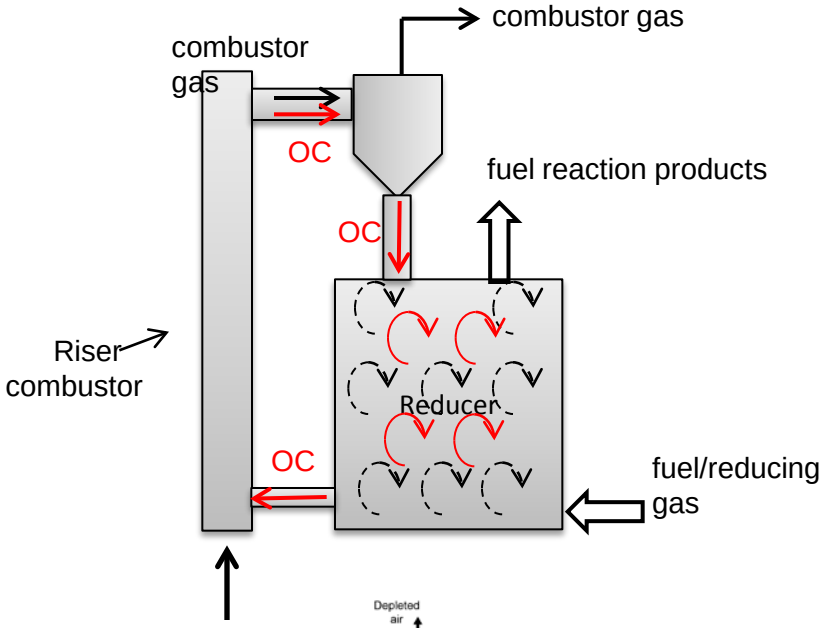
2. Sub-Pilot Unit Operation and Data Crosschecking (OSU)

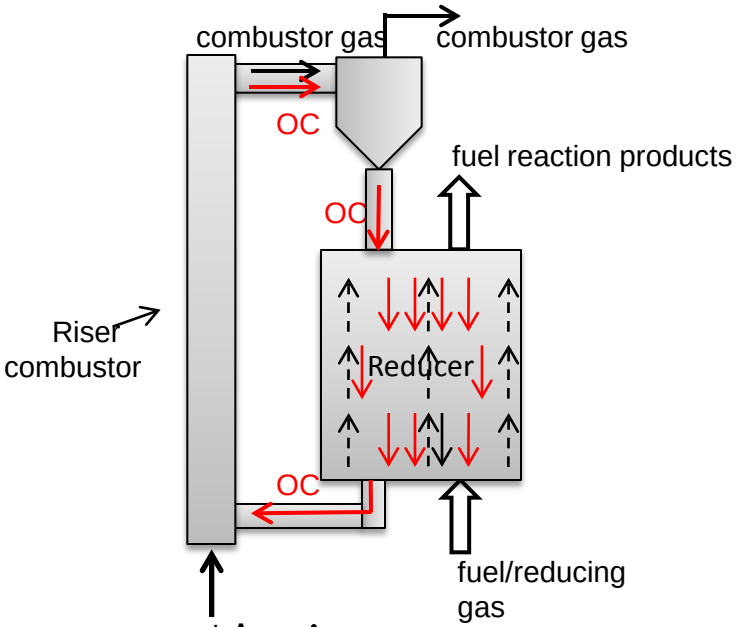
- 300+ hours operation time with encouraging results
- Zone seal concept proved under reactive conditions
- CFD modeling support
- Fluidized bed combustor testing in progress
- Fine removal device tested
- Different types of particles tested

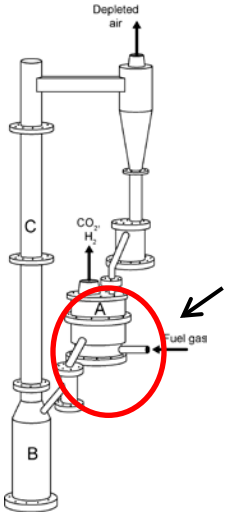
Modes of CFB Chemical Looping Reactor Systems

Mode 1- reducer: fluidized bed or co-current gas-solid (OC) flows

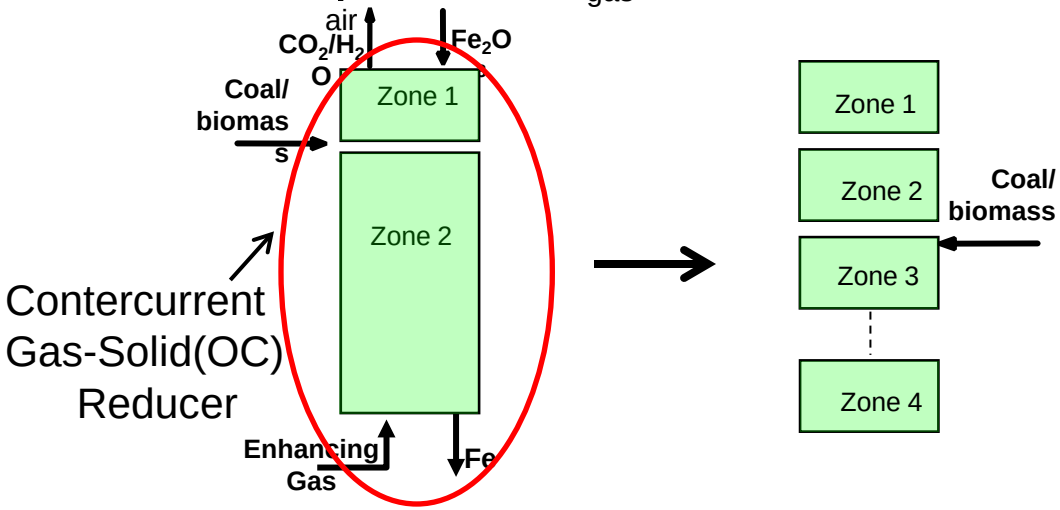
Mode 2 - reducer: gas-solid (OC) counter-current dense phase/moving bed flows







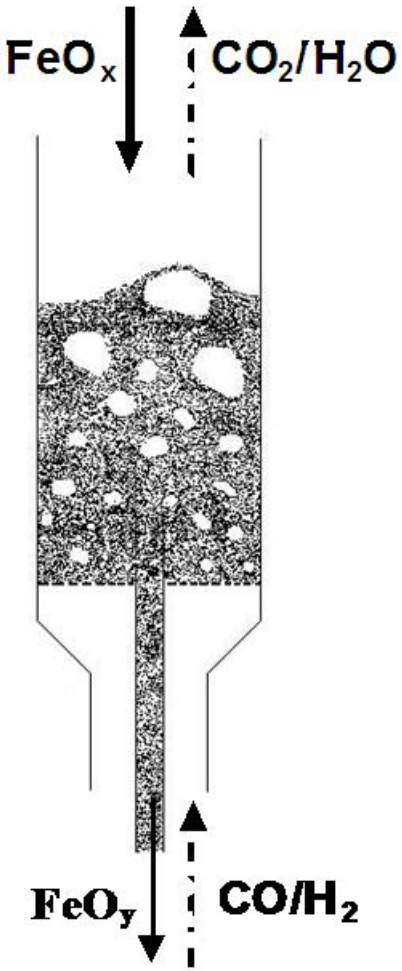
Fluidized Bed Reducer



Chalmers University 10-kW$_{th}$ CLC System

Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

Chemical Looping Reactor Design

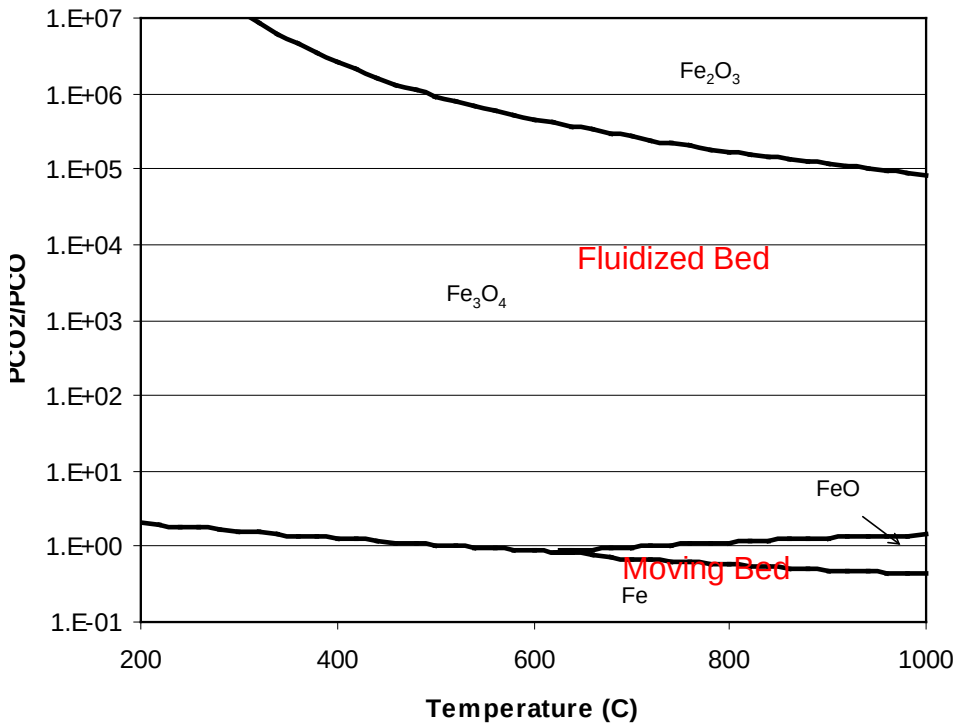


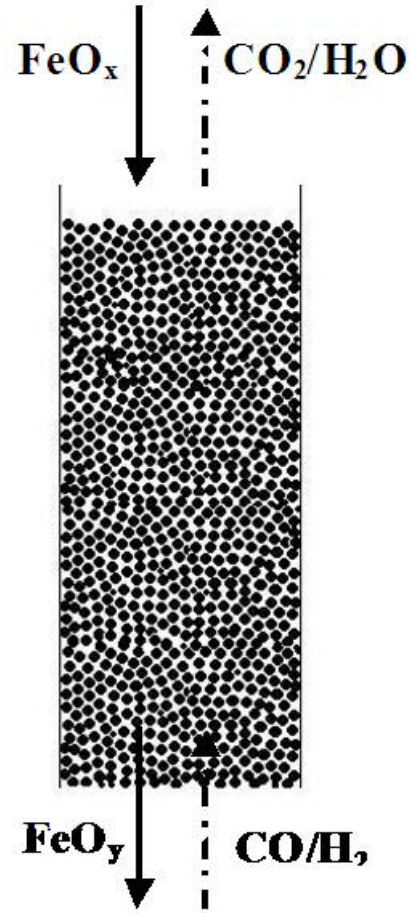
Fluidized Bed

(x>y)

Fluidized Bed *v.s.* Moving Bed

11.11% ←	Maximum Solid Conversion	→ **50.00%**
> U_{mfv} ←	Gas Velocity	→ **< U_{mfv}**
Small ←	Particle Size	→ **Large**





Moving Bed

Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

4000 – 10000 kg/s or 14,000 – 36,000 ton/hour

< 3,000 ton/hour

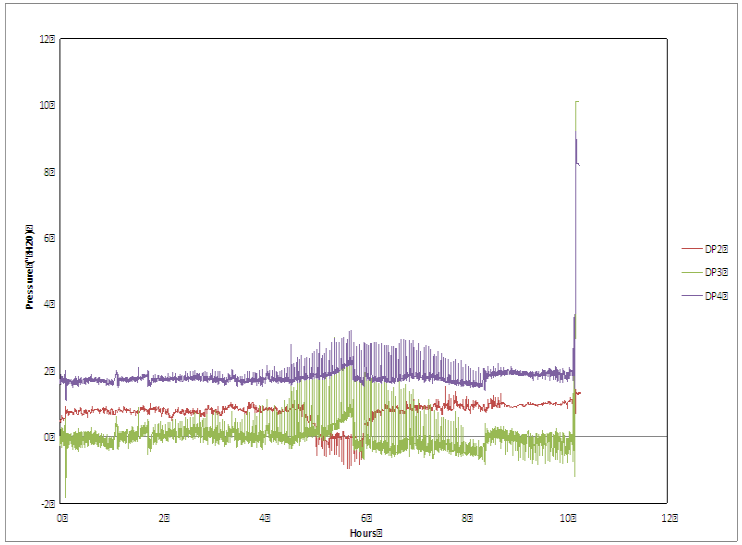
Particle Type	Ni		Cu				
Type of Data	Lab Scale	CFB 120 kW	Lab Scale	CFB 10kW	Lab Scale	CFB 300W	Moving Bed -H_2 25 kW
Particle Type	NiO/ $MgAl_2O_4$	NiO/ $MgAl_2O_4$	CuO/ Al_2O_3	CuO/Al_2O_3	Fe_2O_3/ $MgAl_2O_4$	Fe_2O_3/ Al_2O_3	Composite Fe_2O_3
Air Flow Rate @1000 MWth and 10% Excess (mol/s)	11784						1309
Volumetric Air Flow Rate at 1 atm and 900 ºC (m^3/s)	1134						126
Particle Circulation Rate @ 1000 MWth (*kg/s*)	**4000**	**10000**	**3000**	**6000**	**8000**	**10000**	**800**
Reducer Solids Inventory (tonne)	230	160	70	total 2100	500	1200	1500 Total
Oxidizer Solids Inventory (tonne)	390	80	390		n/a	350	
Medium Particle Size (µm)	153	120	300	200	153	151	2000
Particle Density (g/cm^3)	1.9	5	2.5	2.5	4.1	2.15	2.5
Ut (m/s)	2	0.8	2	1.2	1.1	0.6	11
Uc (m/s)	4	4.8	4.9	4.2	4.8	3.6	4
Use (m/s)	6	6.7	7.5	6.1	6.9	4.9	9.7
Typical Riser Superficial Gas Velocity (m/s)	7.00						12
Bed Area Turbulent Section (if Required) at 1 atm (m^2)	231.47						25.18
Bed Area Required for Riser Section at 1 atm (m^2)	162.03						10.49
Corresponding **Riser Diameter (m)**	**14.37**						**3.66**
Solids Flux at 1 atm (kg/m^2s)	24.69	61.72	18.52	37.03	49.37	61.72	76.23
Number of Beds Needed given 8 m ID Riser	3.23						<1
Number of Beds Needed given 1.5 m ID Riser	91.73						5.94
Ug for a Single 1.5 m ID Riser at 1 atm (m/s)	642.14						71.29
Ug for a Single 8 m ID riser at 1 atm (m/s)	22.58						2.5 (Ug < Ut; N/A)
Required Pressure for a Single 1.5m ID Riser (atm)	91.73						10.00
Solids Flux for a Single 1.5 m ID Riser (kg/m^2s)	2264.69	5661.71	1699	3397.03	4529.37	5661.71	452.88
Required Pressure for a Single 8 m ID Riser (atm)	3.23						Ug < Ut; N/A
Solids Flux for a Single 8 m ID Riser (kg/m^2s)	79.62	199.04	59.71	119.43	159.24	199.04	

25 kW_{th} OSU Sub-Pilot SCL Unit

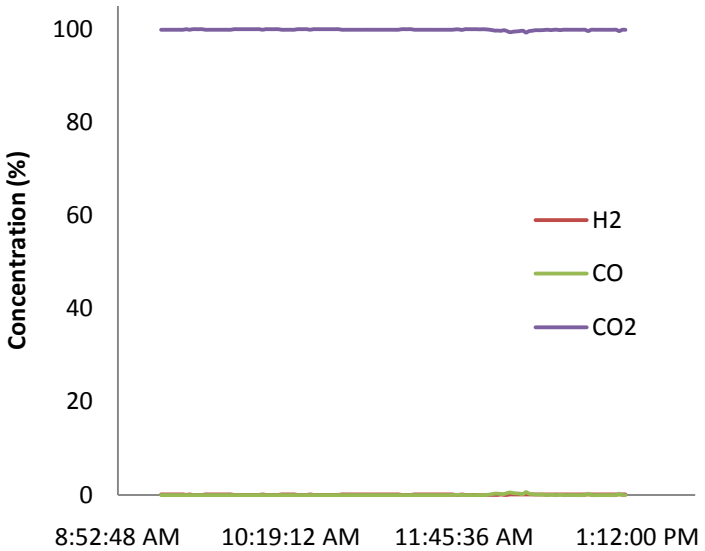
Recent Unit Demonstration

- 300+ hours operation
- Average CO_2 purity generated throughout run > 99%
- >99.99% hydrogen purity at steady state
- Steady Pressure Profile throughout Test run

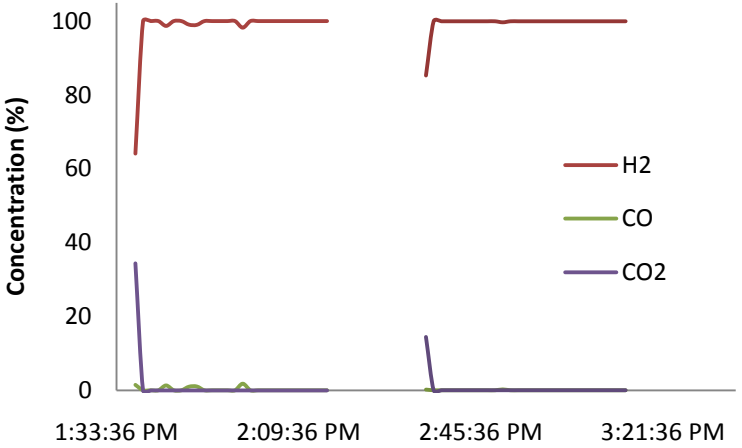
Differential Pressure Profile



Reducer Gas Composition



Oxidizer Gas Composition



Status of the Key Tasks (cont.)

3. Cold Flow Model Study (PSRI, OSU)

- **Cold Model Design and Construction**
  - Design and fabrication completed
  - Shakedown completed with smooth solid flow
- **Cold Flow Model Test**
  - Test matrix developed from hot conditions
  - Both dummy particle and oxygen carrier particle tested
  - Simultaneous operation of 3 zone seals
  - Pressure balance matched with calculation
  - Main loop control is robust and reliable
  - Fulfilled proposed CFM tasks
- **Fine removal device design and test**
  - Several configurations have been designed and tested in cold models
  - Implemented to sub-pilot hot unit test

Status of the Key Tasks (cont.)

4. Pilot Plant Design and Cost Estimate (B&W, OSU)

- **Front End Engineering and Design (FEED)**
  - Design Specification Documents
    - Mechanical specification document
    - Control specification document
  - Preliminary P&ID completed following Class I, Division II safety code
  - Initial cost estimate completed
- **Site Information**
  - Discussed with NCCC for design and safety standards
  - Obtained locations and core samples for modular structure design
- **Detailed P&ID Design and Cost Estimate**
  - Extensive discussion between B&W and OSU
  - Summarized design uncertainties and discussed cost reduction strategies
  - 6 months for detailed pilot plant design and cost estimation

Preliminary Process Hazard Analysis

- Three main segments including utility, primary loop and auxiliary, with more than 40 nodes reviewed
- Trip conditions

Plant Component	Issue	Severity Level	Indication from P&ID	Mitigation Strategy	Shut Down	Shut Down
Bed height monitor	Malfunction	I - III	one of the CS-601-603 doesn't show consistent results with others	1. if we only lose 1 o	Maybe	I
Mainloop	Reactor pressure buildup	II	PIT-420, 490, 530, and 590	Reduce the inlet gas	Maybe	I
Guard Heaters	Heaters do not respond to control	II	TE-500, 400, or 100 irregular	Stop both heaters an	Maybe	I
Particle Makeup	Screw failure/Particle won't feed	II	Bed height drops below CS-603 although particle makeup system is on	replace screw	maybe, depe	I
Electricity	Outage	III	n/a	Southern should miti	Yes	V
Compressed Air	Outage/low pressure	III	1. Southern signal OR 2. PIT-210	Shut down the heatin	Yes	II
Oxygen carrier	Pluggage	III	bed height falls below CS-603	Stop the heaters, flus	Yes	III
Mainloop	Reactor overheat	III	TE-500, 400, or 100 irregular	Turn off all the heatin	Y	III
Bed height Mechanical V	Don't open	III		Stop heating, purge a	Y	III
Zone seals	Pressure imbalance	III	PDIT-350, 351, 360, 361, 370, 371 out of predetermined threshold values	1. install three transd	Maybe	I
Reducer	Oxygen level HH	III	Install continuous gas monitor for O2 only in reducer outlet, all other analy	Switch all the gases	Y	II
Oxidizer	Oxygen level HH	III	Install continuous gas monitor for O2 only in oxidizer outlet, all other analy	Switch all the gases	Y	II
L-Valve	Pressure imbalance	III	Install a new PDIT between the legs PDIT-371 and PIT 100	Increase steam flow,	Y	II
particulate filter	Failure of the filter/particle go Thro	III				
particulate filter	pluggage of filter, pressure buildup	III				
combustor gas cooler	gas doesn't cool down	III	TE-701 high	shut down unit, fix wa	shut down u	I
pressure control valves	doesn't operate	III	PIT and PDITs show unintended results, e.g. when the sequence suppose	adjust the gas flow to	yes	I
back pressure regulator	doesn't hold pressure or shut off	III	PIT and PDITs show unintended results, e.g. when the sequence suppose	adjust the gas flow to	yes	I
flare and thermal oxidize	failure	III	Southern signal	controlled shut down	yes	I
Particle Makeup	gas leakage	II-IV	PIT-810 shows uninteded pressure	add an additional valv	maybe, depe	I
cyclones	lock hopper failature in secondary	II-IV	PIT-710 shows uninteded pressure	add isolation valve rig	most likely r	I
Mainloop	Reactor Rupture	IV	PIT-420, 490, 530, and 590 suddenly decrease, should install some direct	1. check on how PSI	Y	IV
Mainloop	Pressure Relief Valve Rupture	IV	PIT-420, 490, 530, and 590 suddenly decrease, should install some direct	1. no option, just shu	Y	IV
Cooling water	Outage					I
reducer gas cooler	same as above		TE-591 high			I
oxidizer	same as above		TE-491 hgih			I
gas injection valves	talk about it after P&ID is finalized					

On-Going Work from B&W

1. Finalize design of principal-loop components
   - Particle separation
   - Process heaters and coolers
   - Gas distributor
   - Temperature and pressure sensors
2. Finalize design of auxiliary equipment
   - Gas injection system
   - Particle make-up and removal systems
   - Sulfur removal system
3. Heat and Material Balances
4. Review OSU's test matrix
5. Finalize functional specification documents
6. Complete HAZOP review
7. Generate final P&ID and detail design drawings
8. Develop an engineering and construction schedule
9. Provide a final cost estimate

Other Key Tasks

5. Pilot Plant Construction, Shakedown, and Operation
   - Construction starts in 1Q 2012
   - Shakedown by 4Q 2012
   - Pilot plant operation starts by 1Q 2013
6. Process Analysis and Commercialization Plan
   - 2013

Upcoming large-scale demonstrations of chemical looping technology

Organization/Location	Process	Size	Features
HUNOSA, Spain	$CaCO_3$ – CaO (CaOling) looping for post **combustion** CO_2 capture	2 MW_{th}	CO_2 is from the flue gas generated from 50 MWe coal power plant .
Technical University of Darmstadt, Germany	$CaCO_3$ – CaO (LISA) looping for post **combustion** CO_2 capture	1 MW_{th}	Capture plant is an extension to a 1052 MWe hard coal-fired power plant; carbonator and calciner both are CFBs.
Technical University of Darmstadt, Germany	ECLAIR – ilmenite Redox with coal for looping **combustion** application	1 MW_{th}	Solid fuel conversion use s a fluidized bed reducer operated in a CFB looping system
Alstom, U.S.	$CaCO_3$ – CaO looping for CO_2 capture /$CaSO_4$ –CaS redox with coal for looping **combustion** application	3 MW_{th}	Process uses two calcium –based loop s in a chemical Looping system
OSU, U.S.	Iron based oxygen carrier redox with gaseous fuels for H_2 production in a Syngas Chemical Looping (SCL) **gasification** process	250 kW_{th}	High pressure SCL enables high purity H_2 generation with also high purity CO_2 generation using a counter-current moving bed reactor

Acknowledgements

- ARPA-E/U.S. Department of Energy (USDOE)
- Ohio Coal Development Office (OCDO) of the Ohio Air Quality Development Authority (OAQDA)
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