Chemical Looping Technology for Fossil Energy Conversions

by

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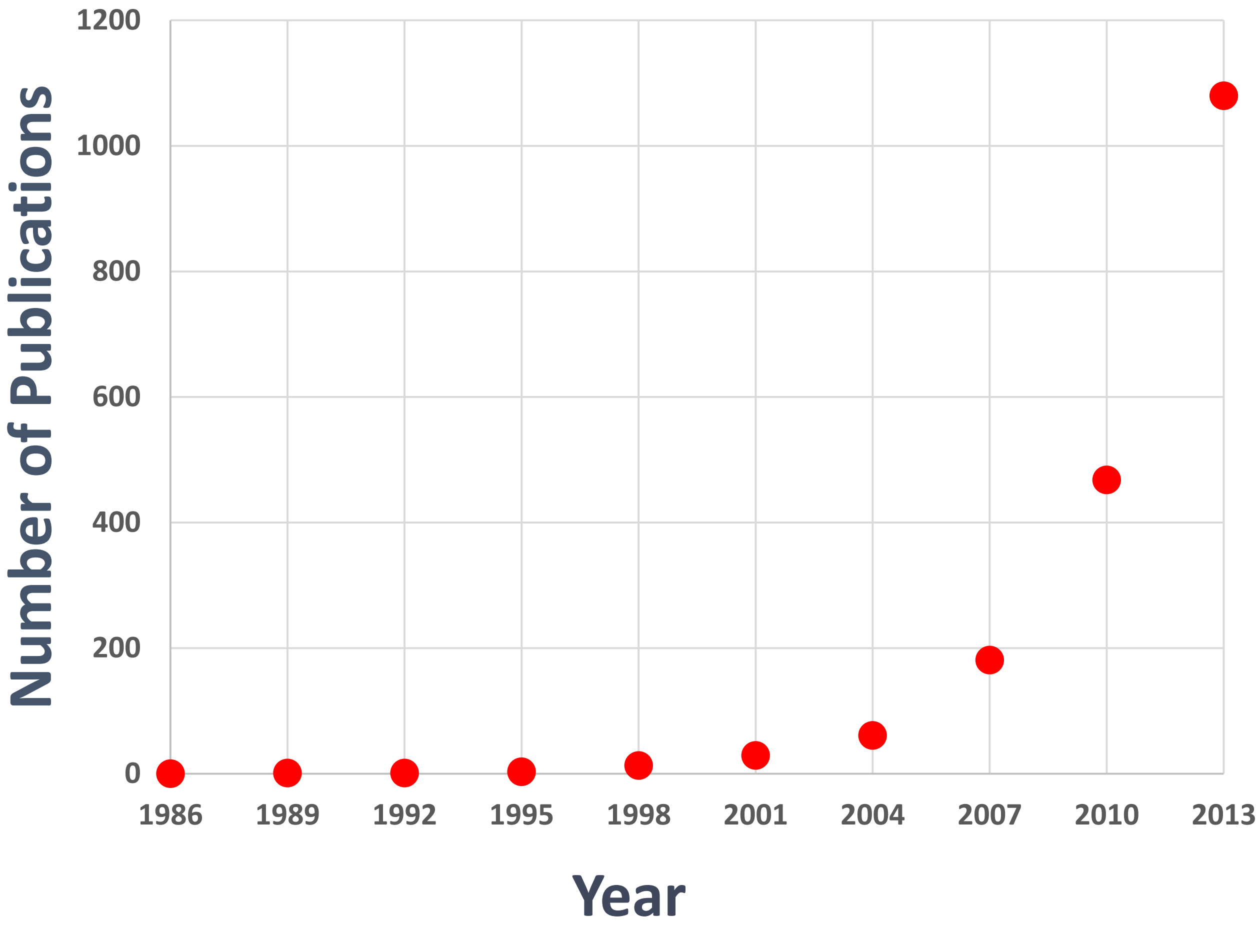
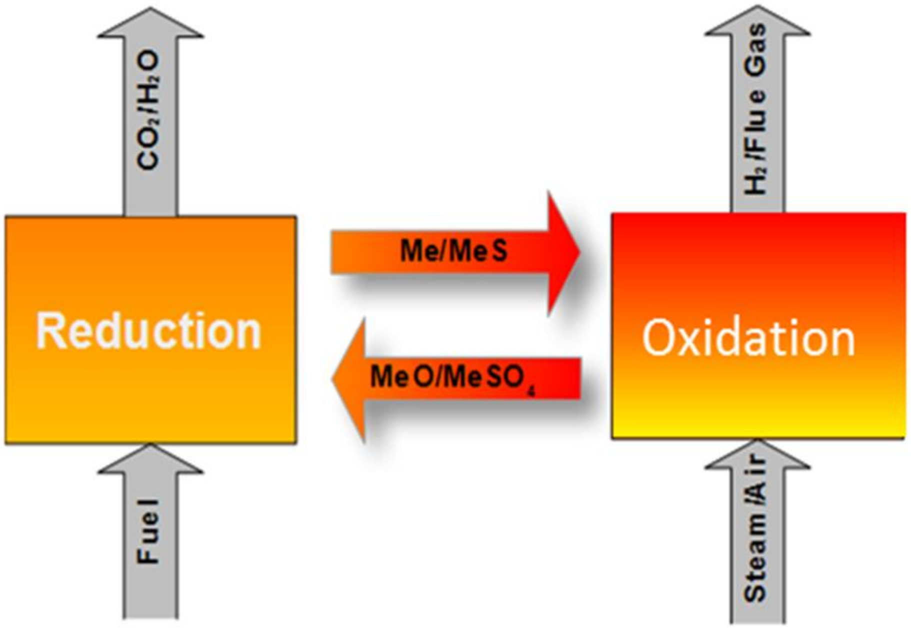
Number of Publications with "Chemical Looping" in the Titles on Google Scholars

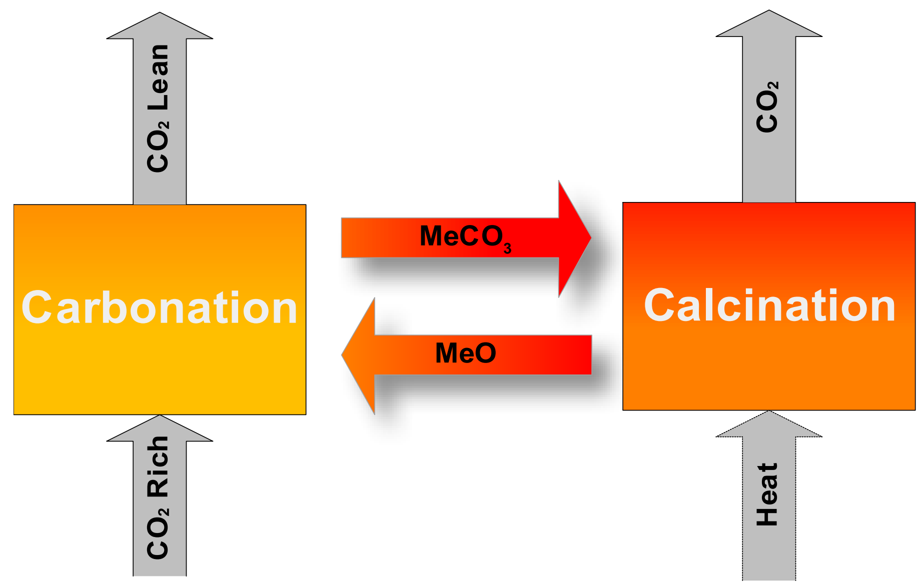


Chemical Looping Systems with CO_2 Generation or Separation

Two typical types of looping reaction systems

Oxygen Carrier (Type I)	CO_2 Carrier (Type II)
Me/MeO, MeS/$MeSO_4$	MeO/$MeCO_3$

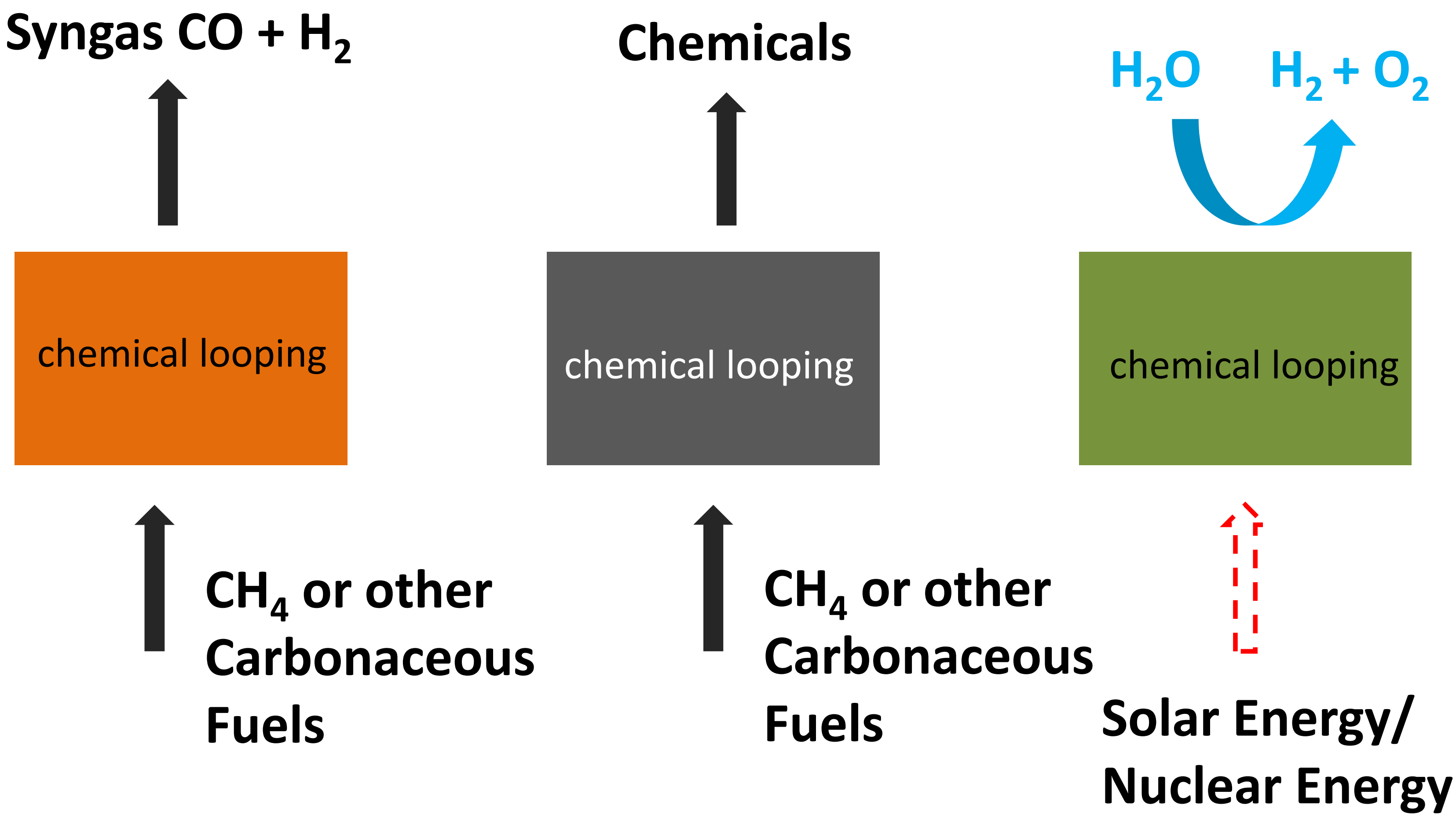




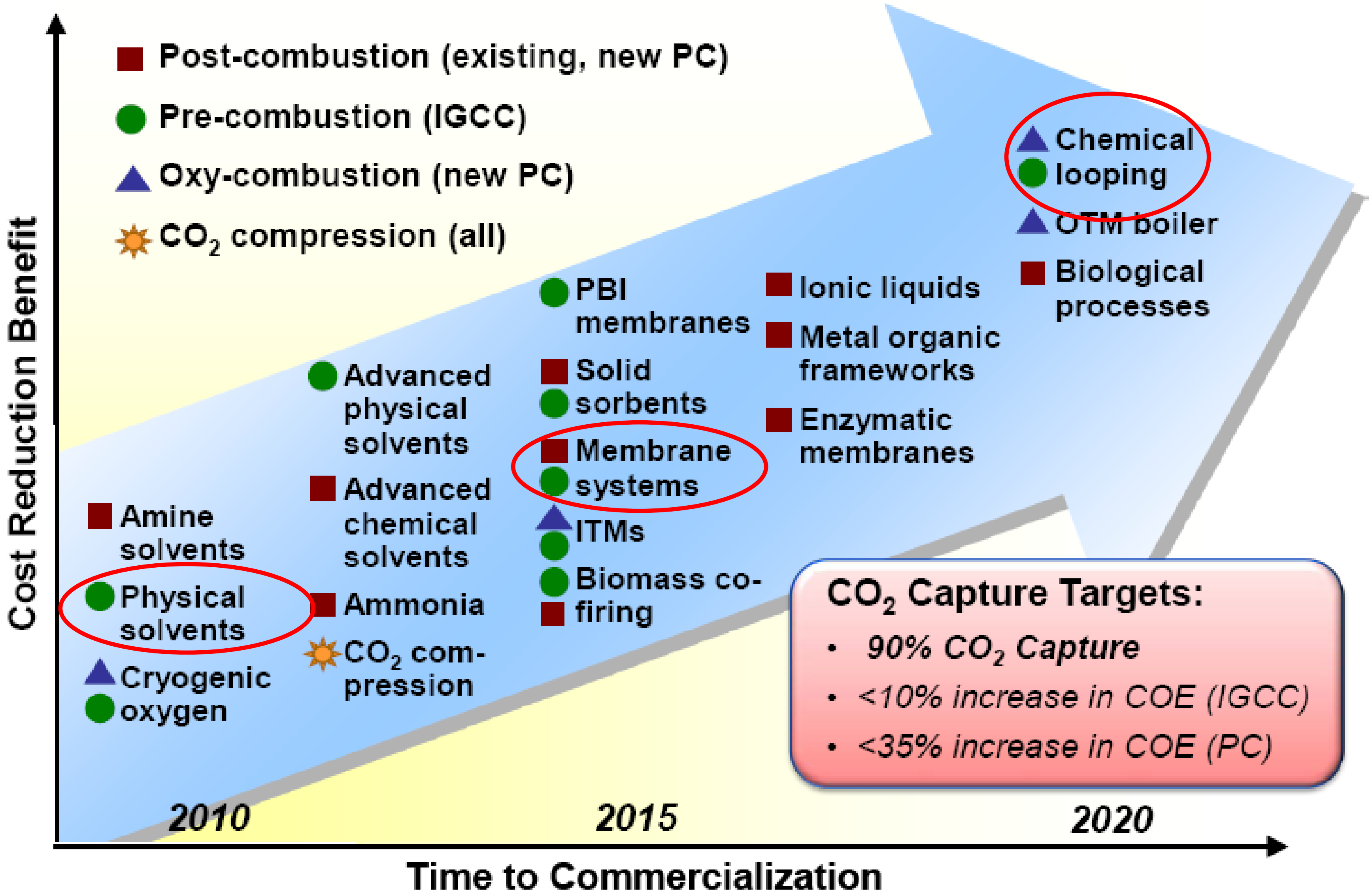
"1st International Conference on Chemical Looping", Lyon, France, March 17-19 (2010).

"1st Meeting of High Temperature Solids Looping Cycle Network", Oviedo, Spain, September 15-17 (2009).

Chemical Looping Systems with Non-CO_2 Generation

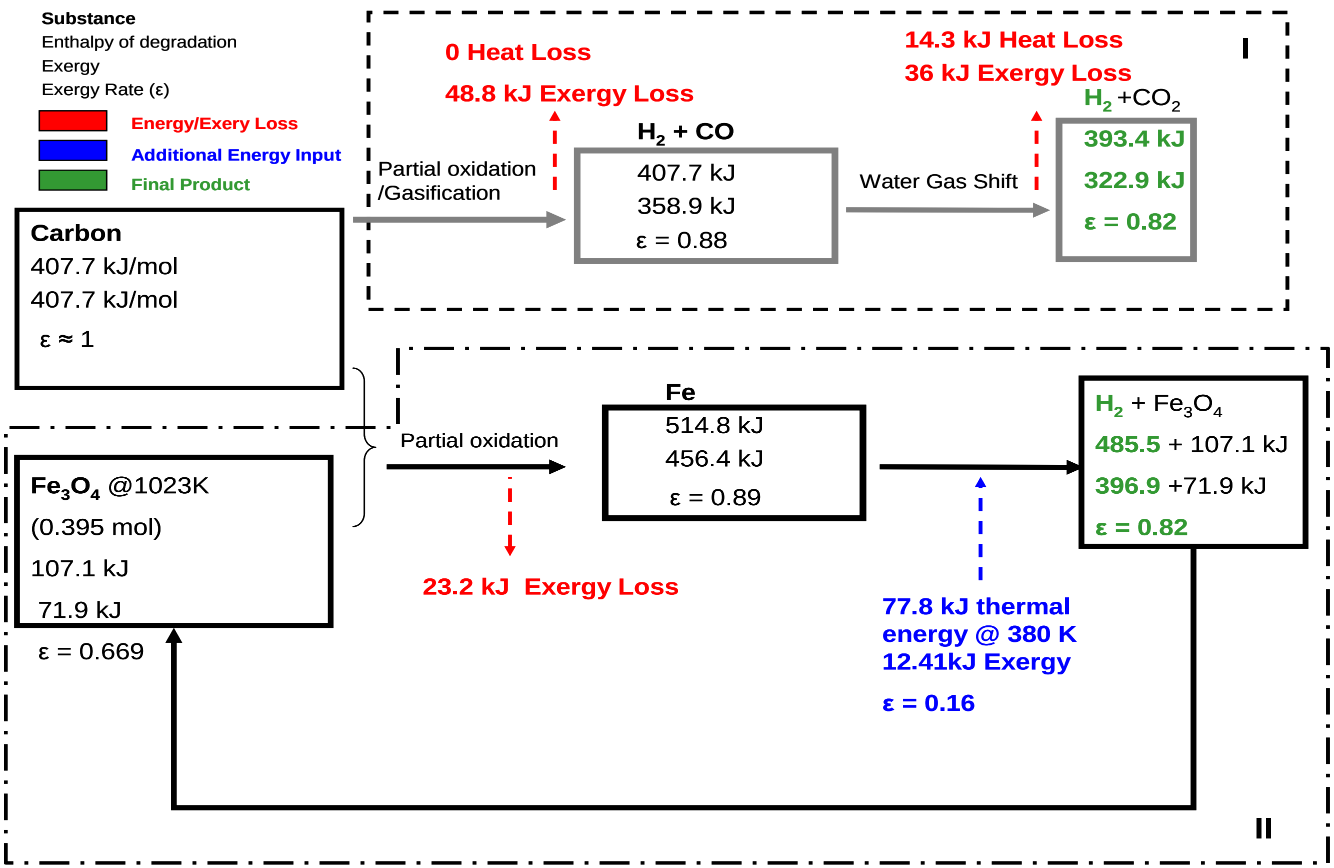


CO_2 Capture from Fossil Energy – Technological Solutions



Source: José D. Figueroa, National Energy Technology Laboratory (NETL), USDOE

Exergy Analysis on Hydrogen Production



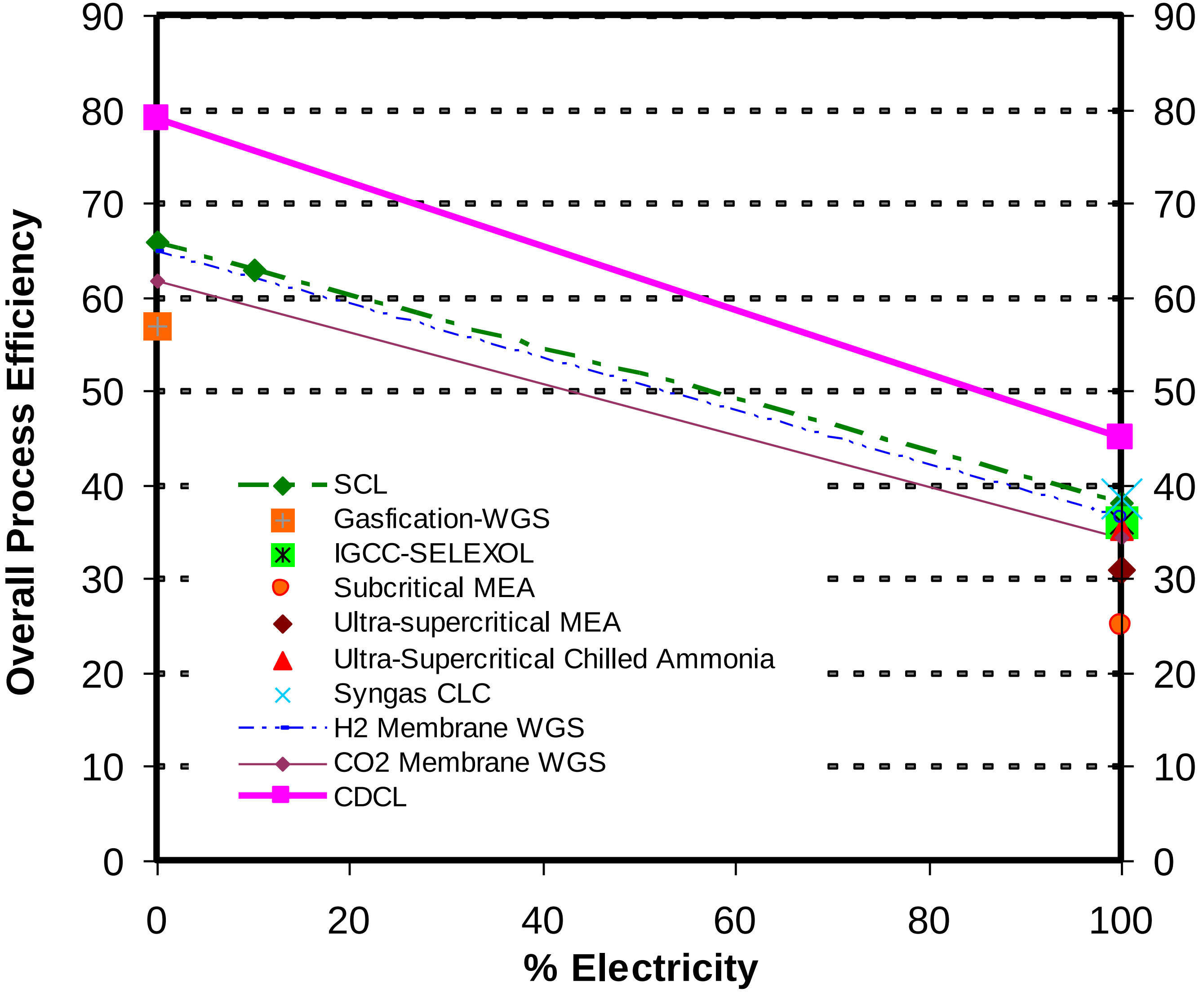
I. Contional Process Exergetic Efficiency

322.9/407.7 = 79.2%

II. Chemcial Looping Process Exergetic Efficiency

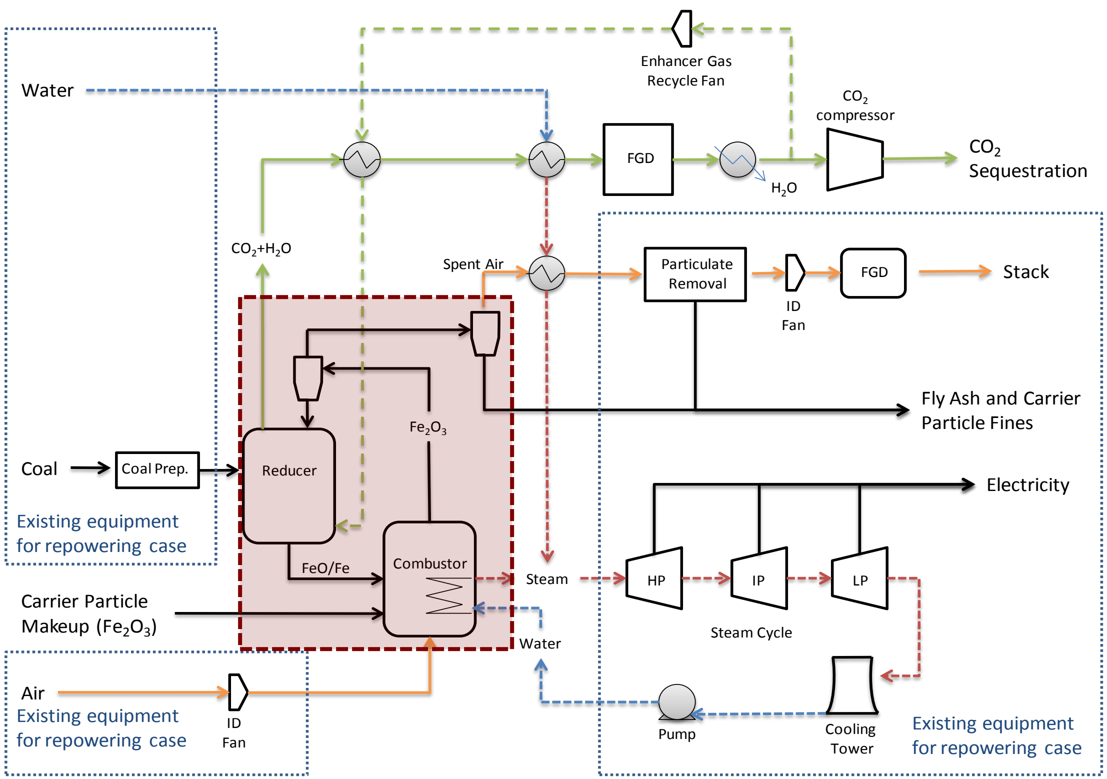
396.9/(407.7 + 12.41)=94.5%

Comparison of OSU SYNGAS and Coal Direct Chemical Looping (CDCL) Processes with Traditional Coal to Hydrogen/Electricity Processes



Assumptions used are similar to those adopted by the USDOE baseline studies.

Economics of Chemical Looping Process



	Base Plant	MEA Plant	CDCL Plant
First-Year Capital ($/MWh)	31.7	59.6	44.2
Fixed O&M ($/MWh)	8.0	13.0	9.6
Coal ($/MWh)	14.2	19.6	15.9
Variable O&M ($/MWh)	5.0	8.7	8.7
TOTAL FIRST-YEAR COE ($/MWh)	**58.9**	**100.9**	**78.4**

Δ = +71%

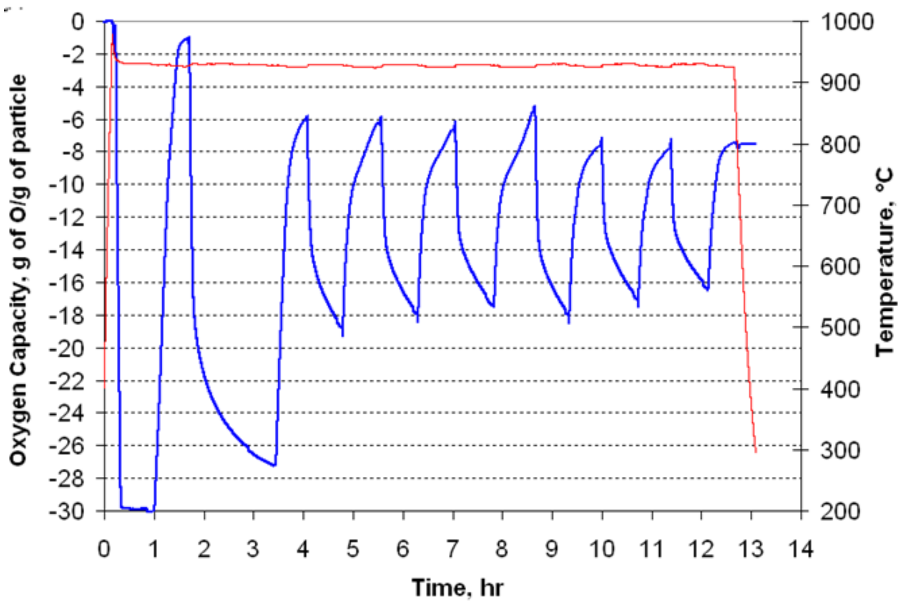
Δ = +33%

- Retrofit to conventional coal combustion process
- CDCL replaces existing PC boiler
  - Additional equipment for CO_2 compression and transportation required
- Techno-Economic analysis performed comparing CDCL to Base Plant with no CO_2 capture and 90% CO_2 capture via post-combustion MEA process

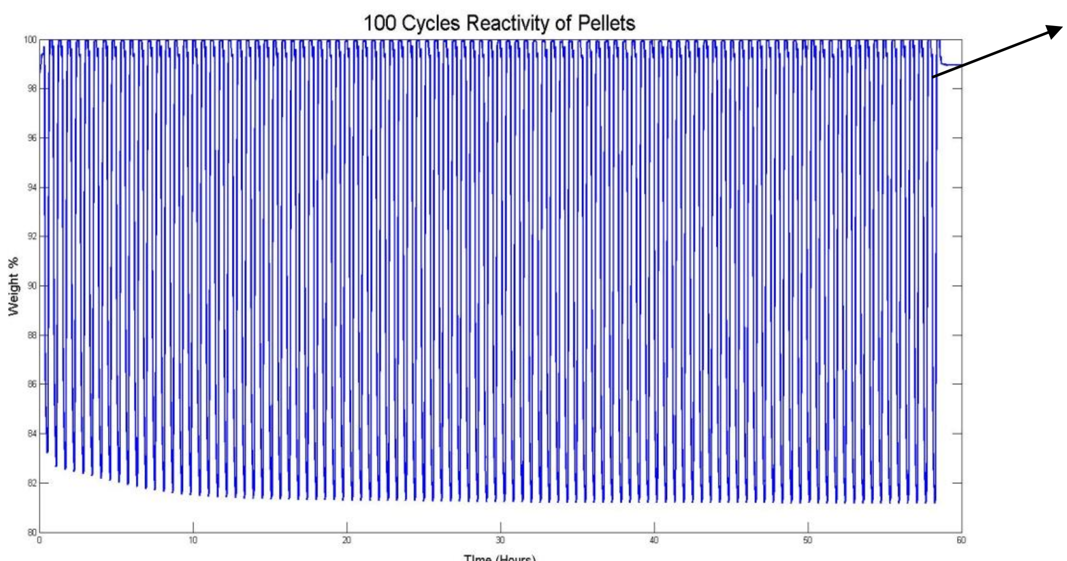
Thomas, T., L.-S. Fan, P. Gupta, and L. G. Velazquez-Vargas, "Combustion Looping Using Composite Oxygen Carriers" U.S. Patent No. 7,767,191 (2010, priority date 2003)

The CDCL process can be also used for high efficient hydrogen production

Cyclic Redox of Pure Fe_2O_3 with Hydrogen

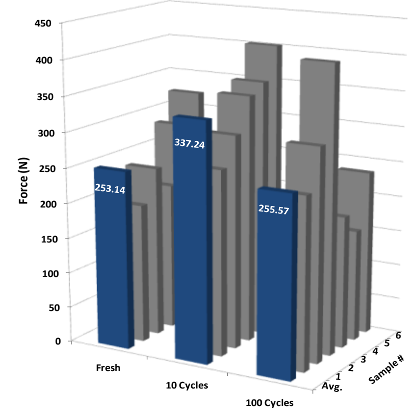


Cyclic Redox of Composite Fe_2O_3 with Hydrogen



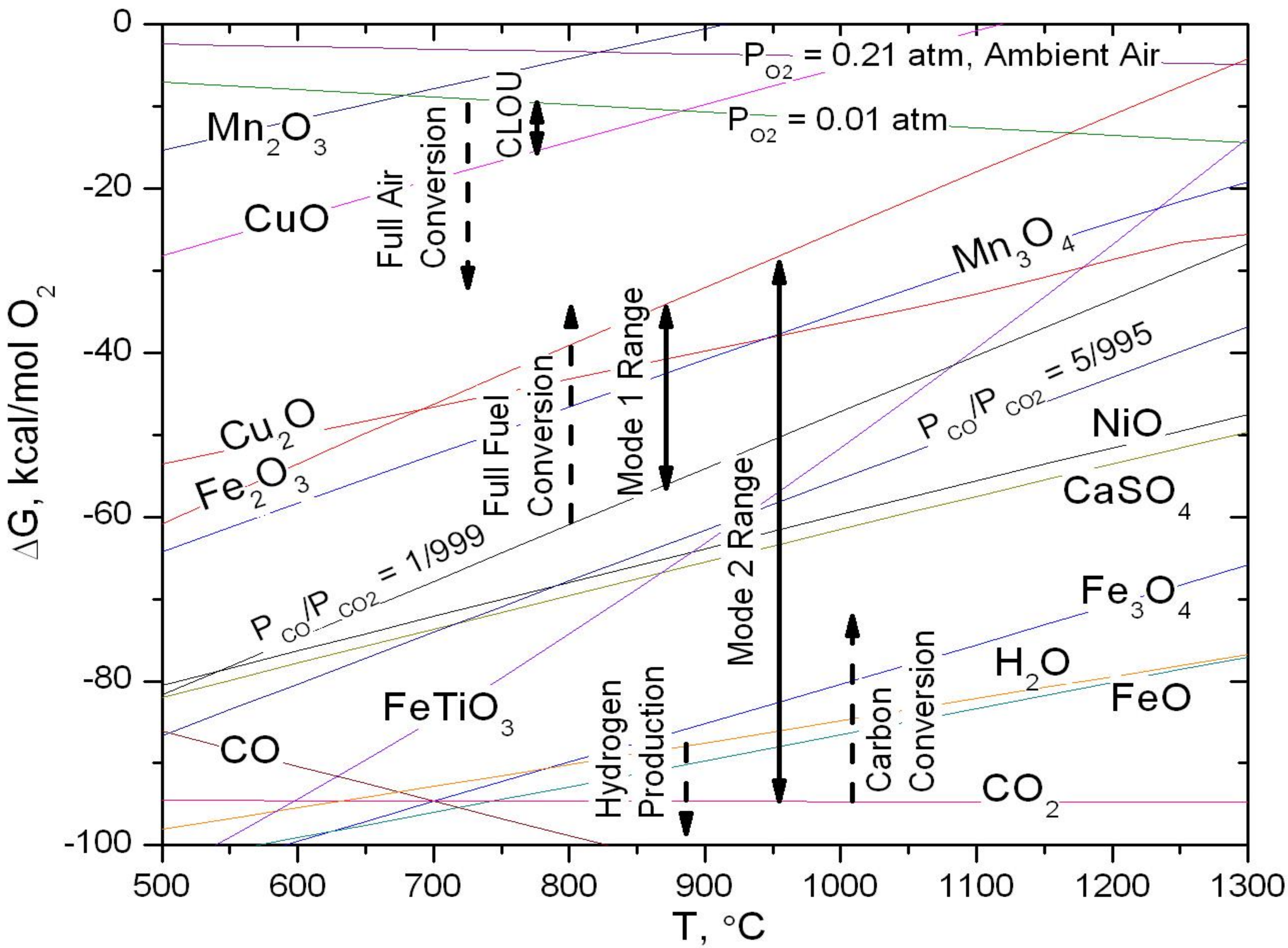
100 Cycle Pellet Reactivity

100 Cycle Pellet Strength

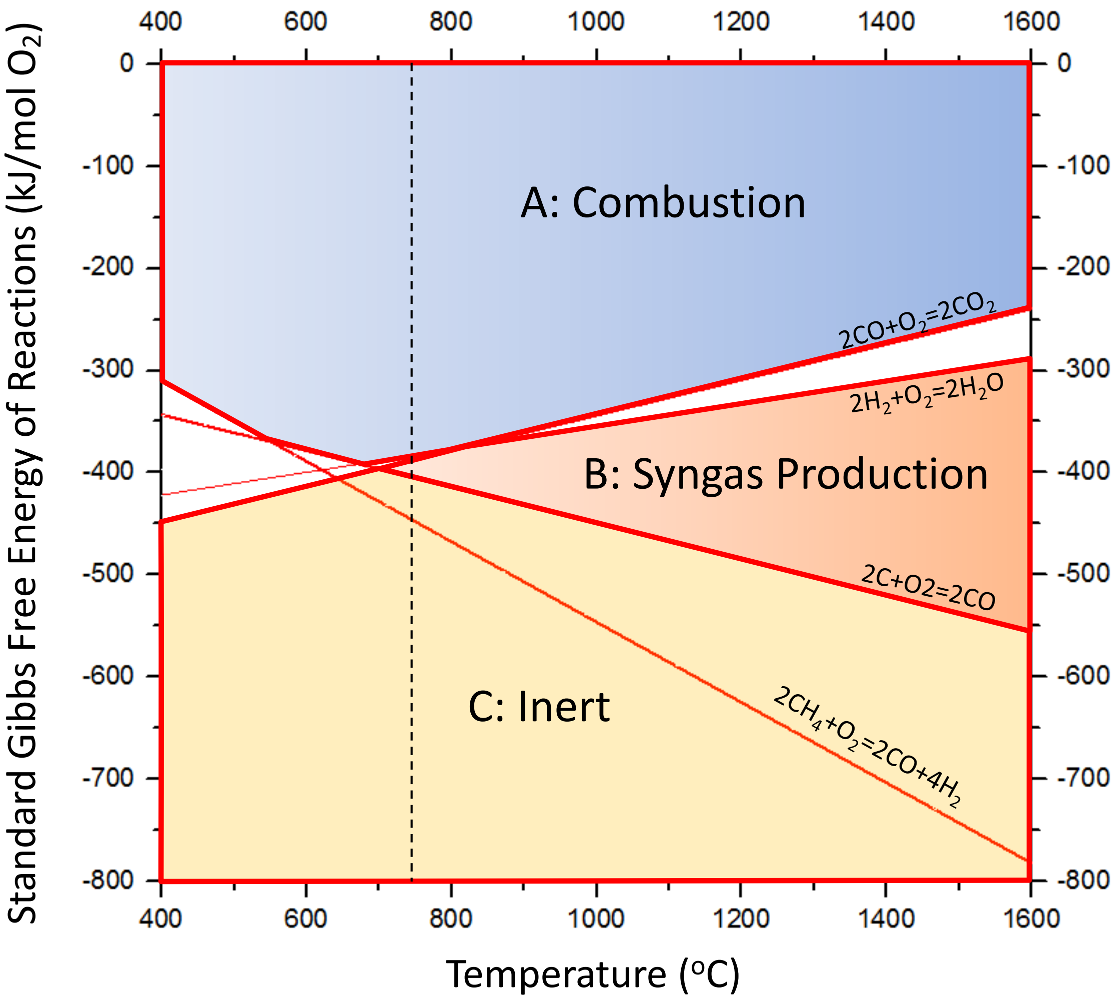


Oxygen Carrier Particle Development

Ellingham Diagram: Selection of Primary Metal



Zones of Metal Oxides for Chemical Looping



Recent research focus on **Complex Metal Oxides**

Zone A: They can work as oxygen carriers for both CLFO and CLPO. (NiO, CuO, CoO, Fe_2O_3, and Fe_3O_4, etc.)

Zone B: They are able to work as oxygen carriers for CLPO but not for CLFO (CeO_2, FeO, etc.)

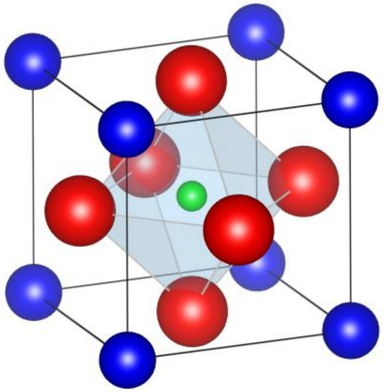
Zone C: They cannot be used as oxygen carriers and are considered as inert materials. (Cr_2O_3 and SiO_2, etc.)

Transition Zone: They are considered as possible CLPO materials with a significant amount of H_2O generated. (SnO_2, etc.)

Complex Metal Oxide Materials

Perovskite Type

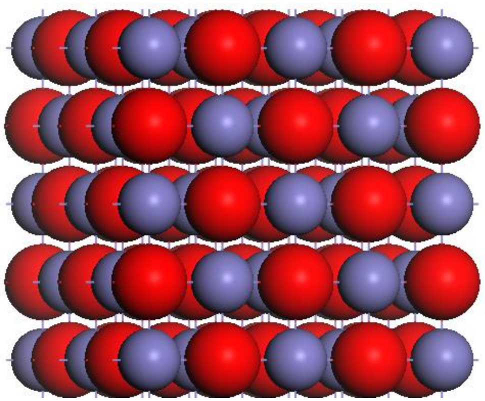
1. Perovskite materials have been considered as promising oxygen carrier materials for both CLFO and CLPO.
2. Perovskite structures are selected in light of their oxygen nonstoichiometry and fast oxygen diffusion features.
3. Partial substitutions of atoms in B sites were found to result in improved catalytic effects.
4. Examples:



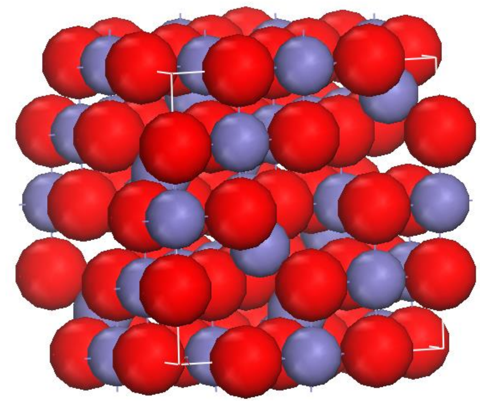
$CaMnO_{3-\delta}$: can release oxygen at high temperatures;
has a high mechanical strength;
high melting point;
low cost (can be synthesized from CaO and MnO_x).
Not stable over long term (decompose to $CaMn_2O_4$ and $Ca_2MnO_{4-\delta}$) in reduced environment

Structures of Iron Oxide

FeO

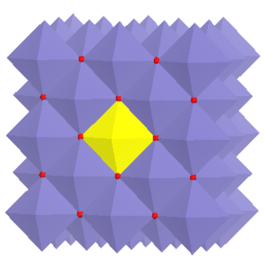


Fe_3O_4



NaCl Type

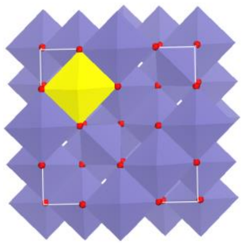
- oxygen close-packed cubic pattern
- iron occupy all **octahedral** interstices



inverse Spinel Type

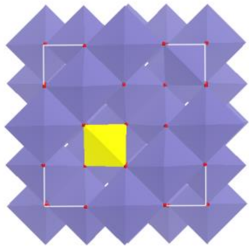
octahedral interstices

1/2 occupation rate

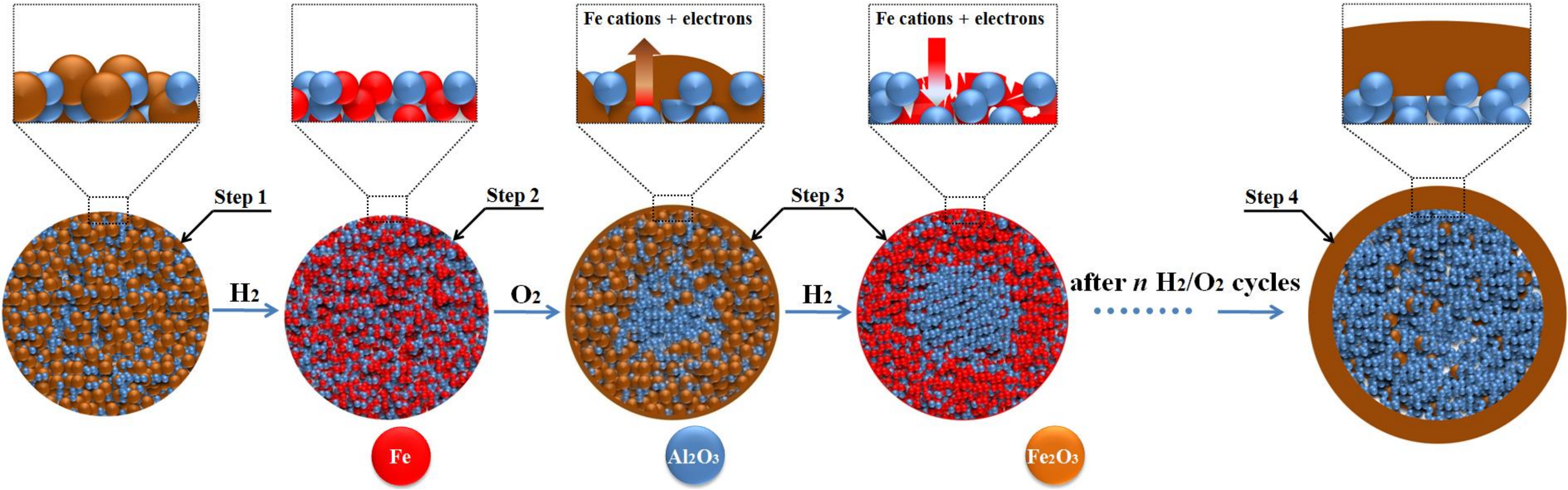


tetrahedral interstices

1/8 occupation rate



Core-Shell Particle Formation through Cyclic Gas-Solid Reactions



$$4Fe_{(s)} + 3O_{2\,(g)} \rightarrow 2Fe_2O_{3\,(s)} \quad (1)$$

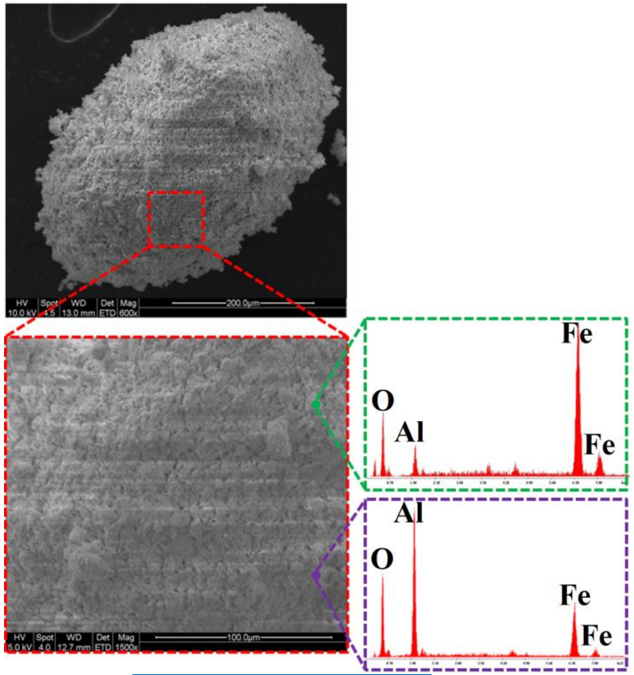
$$Fe_2O_{3\,(s)} + 3H_{2\,(g)} \rightarrow 2Fe_{(s)} + 3H_2O_{(g)} \quad (2)$$

If the cyclic reactions proceed through Fe cation diffusion, core-shell structure forms, *e.g.* Fe_2O_3 + **Al_2O_3**.

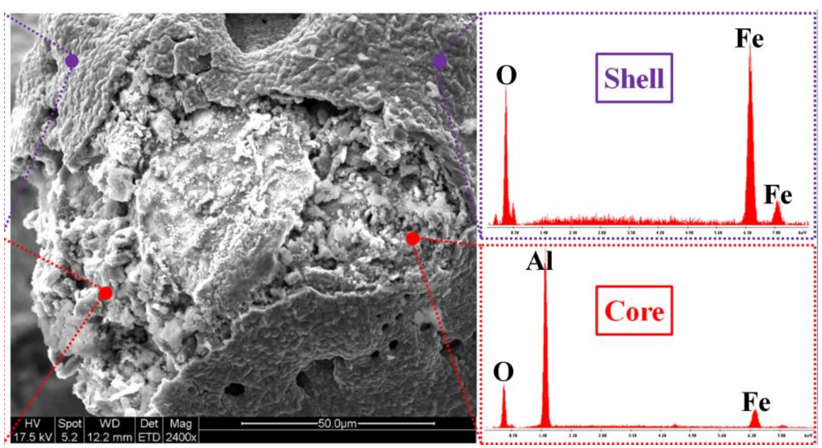
If the cyclic reactions proceed through O anion diffusion, core-shell structure does not forms, *e.g.* Fe_2O_3 + **TiO_2**.

*Al_2O_3 is only a physical support, while TiO_2 alters the solid-phase ionic diffusion mechanism

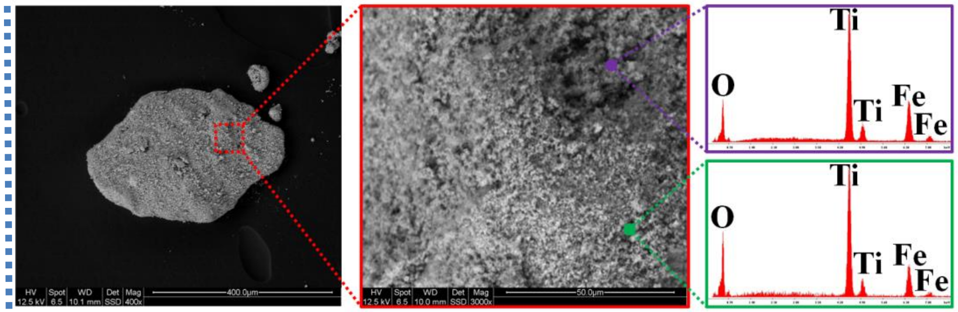
Fe_2O_3+Al_2O_3 VS Fe_2O_3+TiO_2



after 50 redox cycles

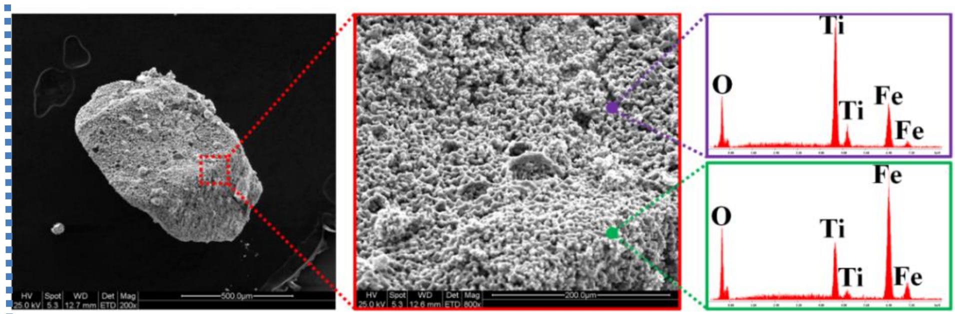


Raw TiO_2-Supported Particle

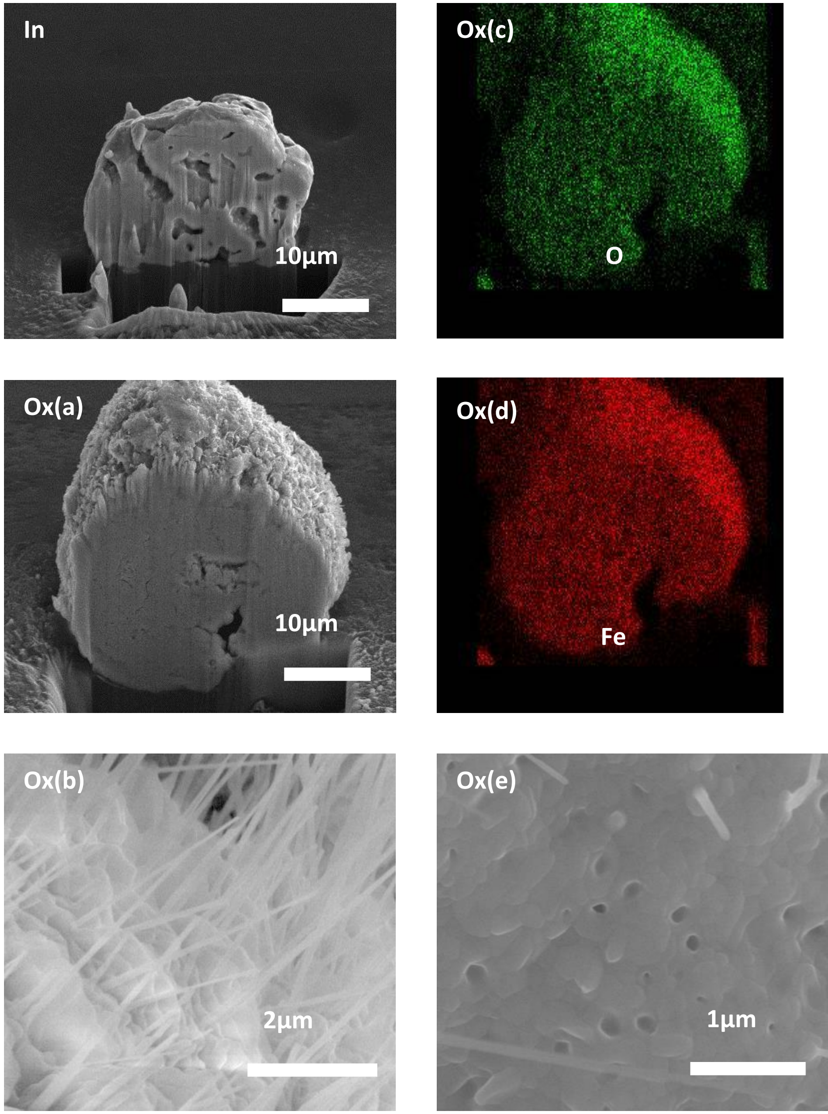


after 50 redox cycles

TiO_2-Supported Particle after 50 Redox Cycles



Single Metal: Iron Microparticles



Oxidation: consumption of oxygen vacancies

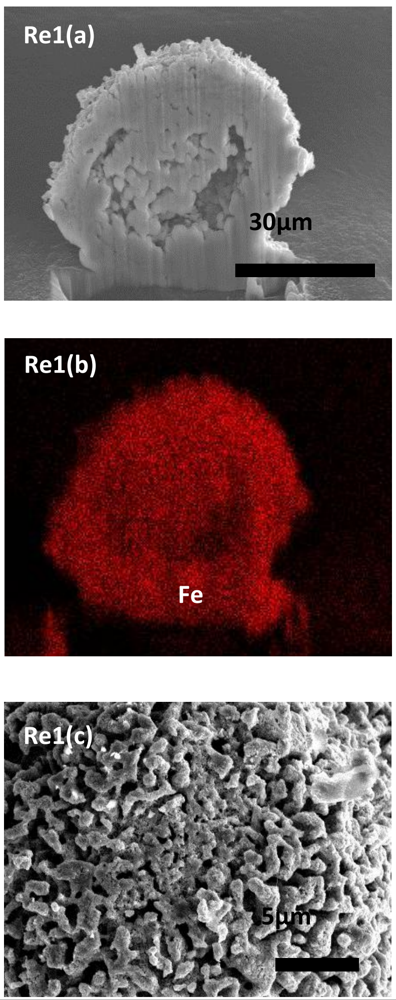
$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} = O_O^X + 2h$$

- Higher outward Fe diffusion coefficient
- Volume expansion of Fe oxidation
- Vacancy condensation at dislocations

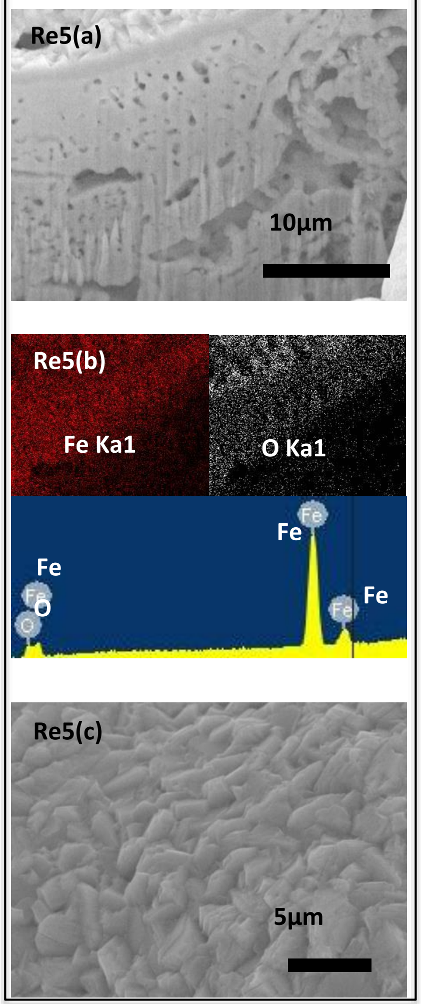
In = Initial particle
Ox = oxidized particle

Single Metal: Iron System

1 cycle



5 cycles

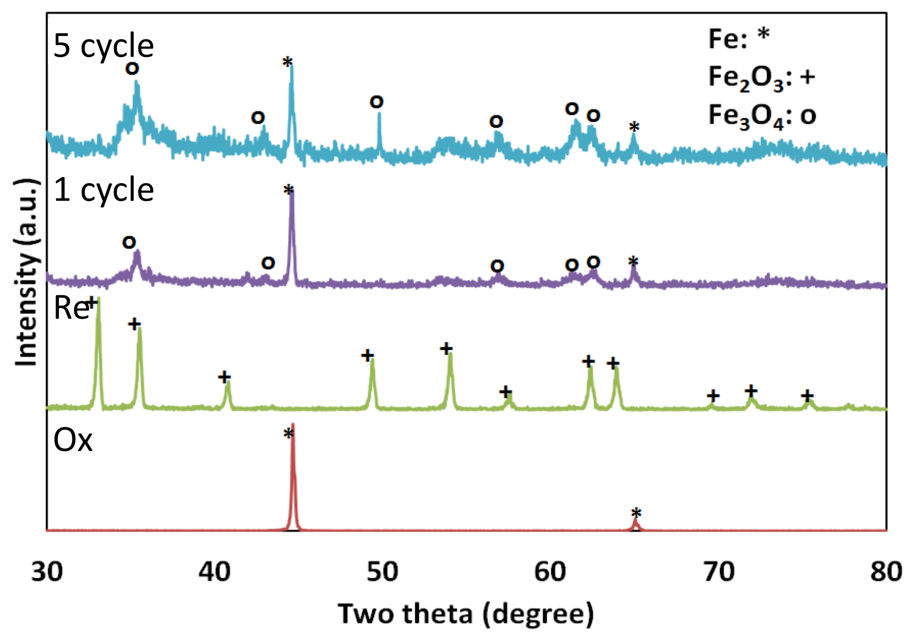


Re = reduced

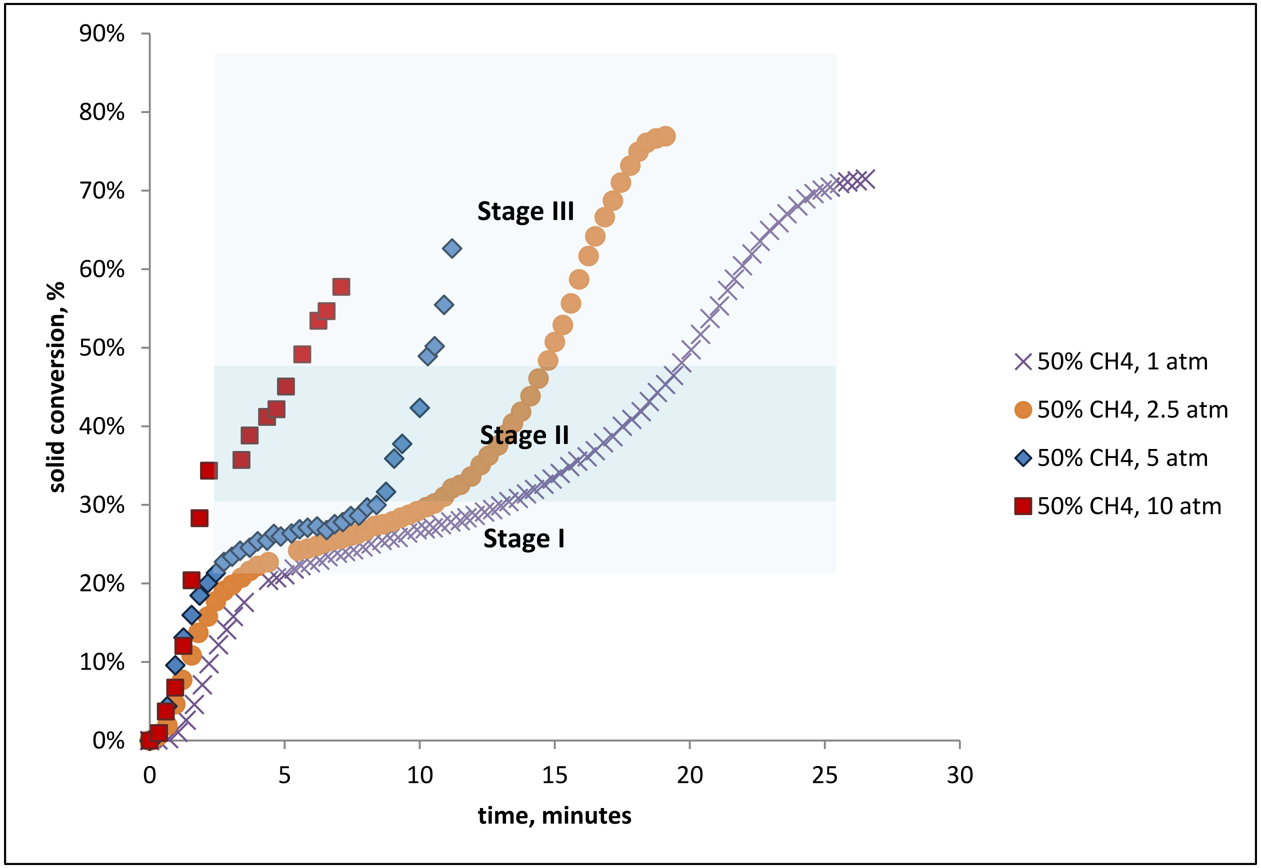
Reduction: Creation of oxygen vacancies

$$O_O^X = ½O_2 + V_{\ddot{O}} + 2e$$

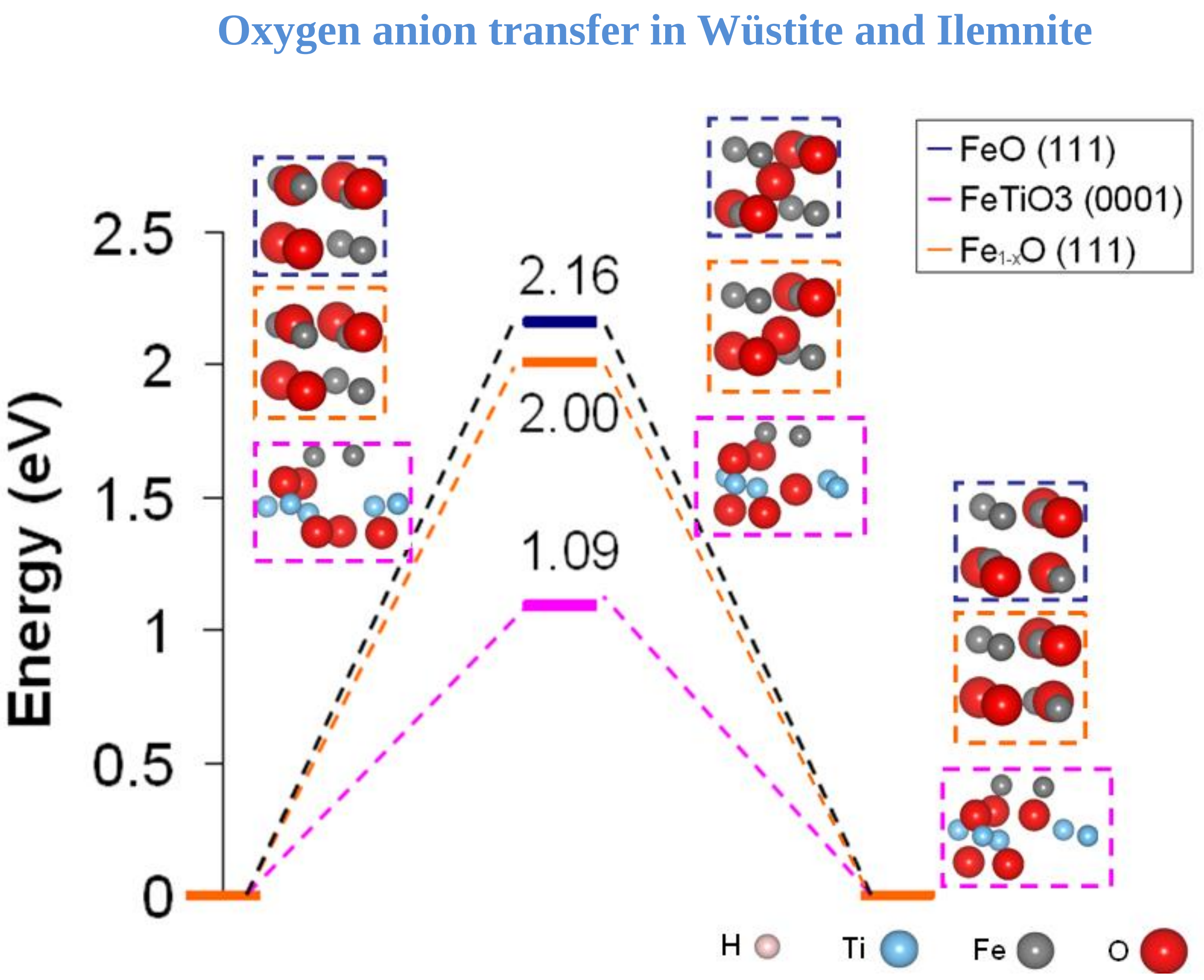
High temperature: sintering effect



Solid reduction conversion with methane effect of pressure



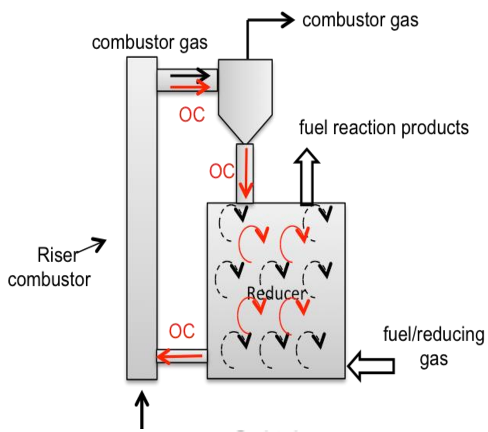
Role of Support – Oxidation of Fe and Fe/TiO_2 DFT Calculation

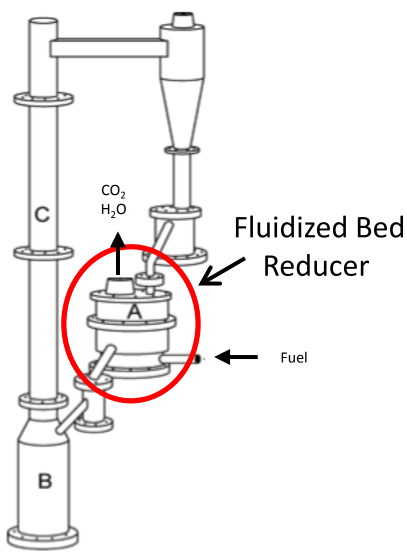


Energy barrier for O^{2-} can be reduced after support addition

Modes of CFB Chemical Looping Reactor Systems

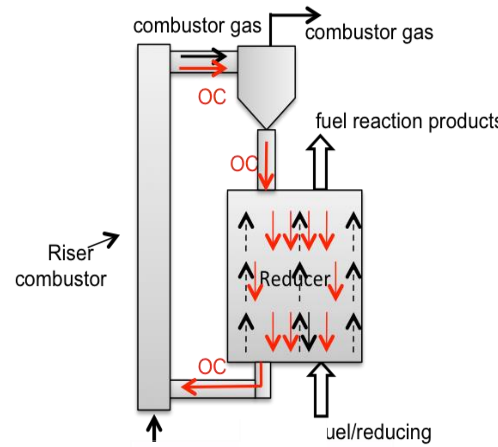
Mode 1- reducer: fluidized bed or co-current gas-solid (OC) flows

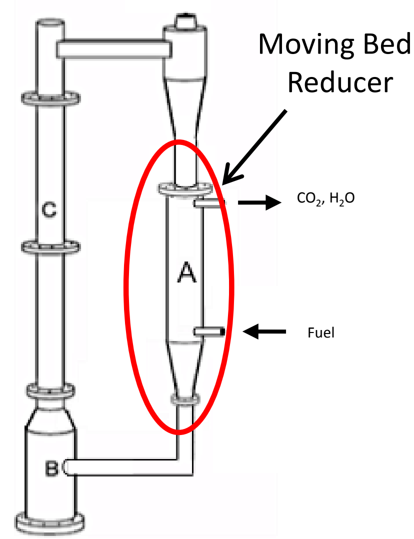




Chalmers University CLC System

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

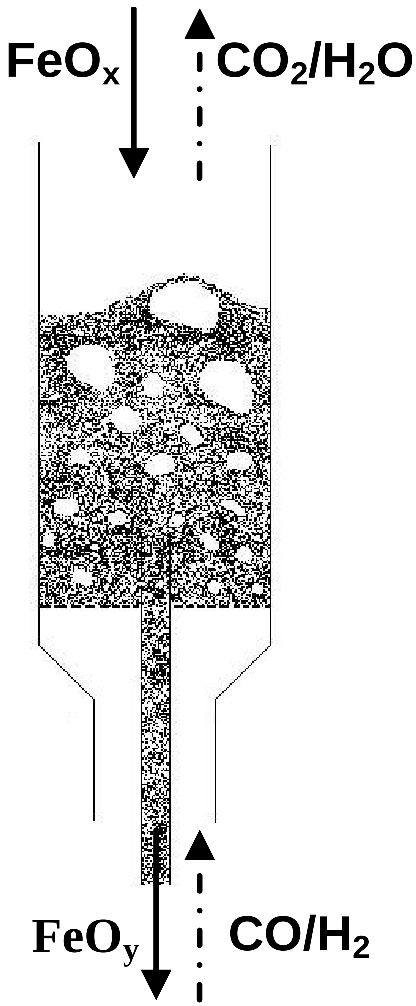




OSU CLC System

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

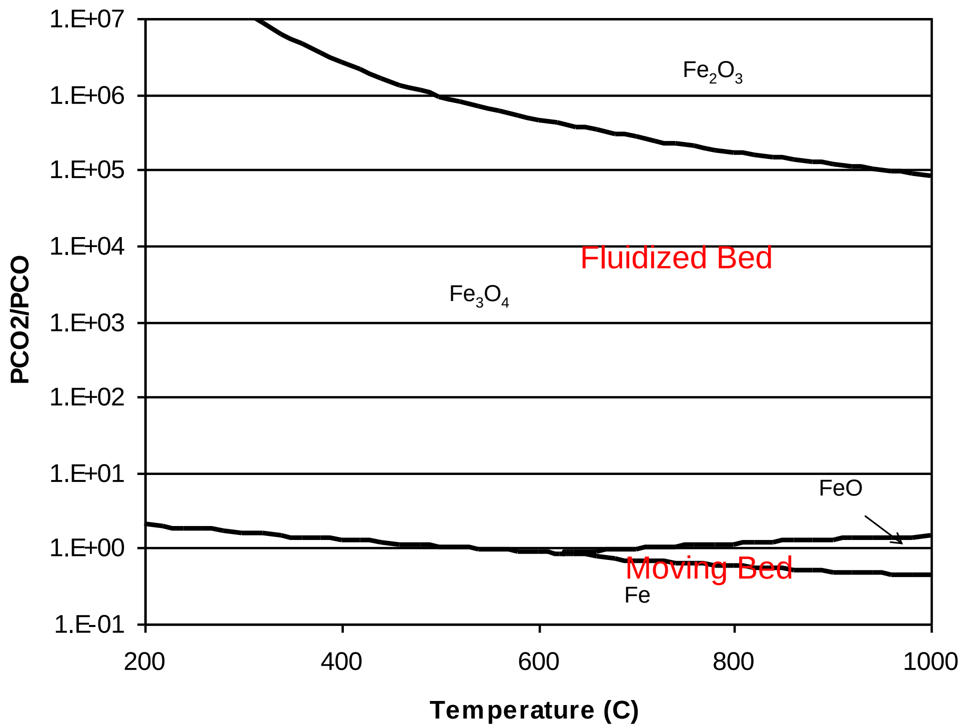


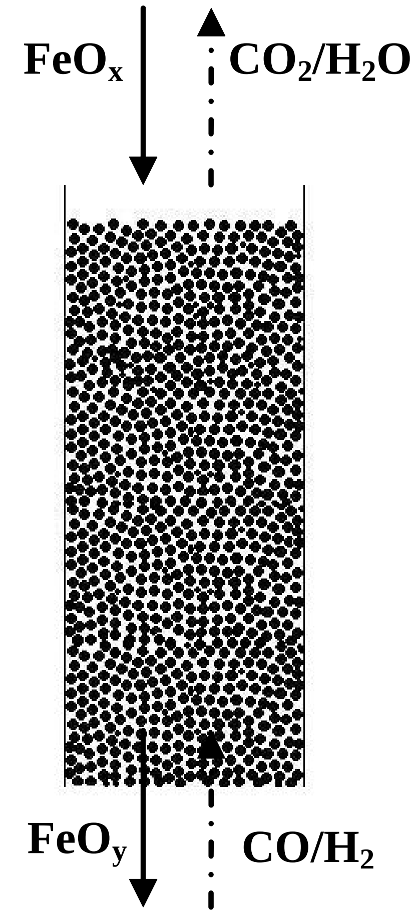
Fluidized Bed

(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**





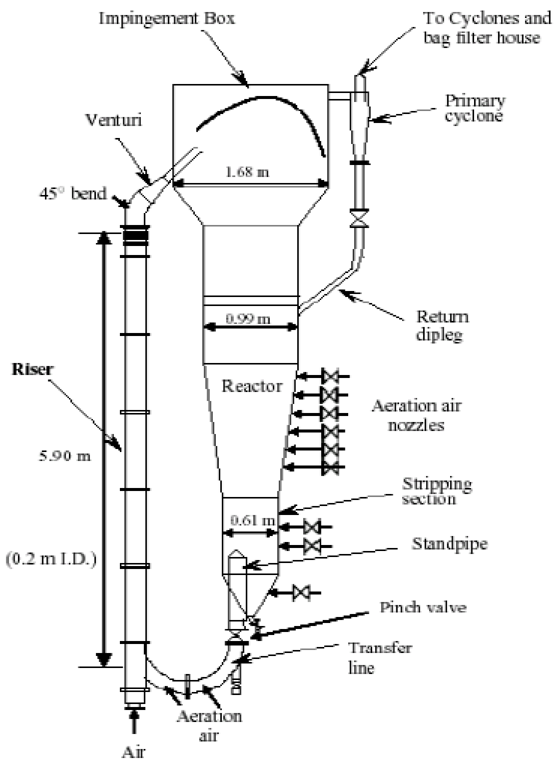
Moving Bed

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

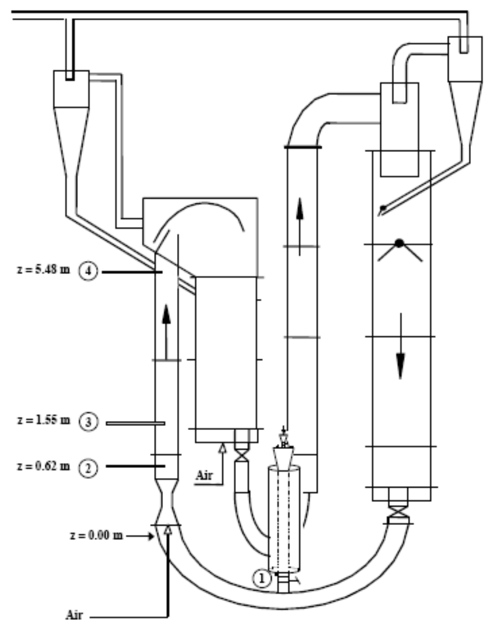
< 3,000 ton/hour

Particle Type	Ni		Cu				
Type of Data	Lab	CFB 120	Lab			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						22 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	

Circulating Fluidized Bed Systems for Chemical Looping Reaction Applications



Single Loop High Density CFB System (Kirbas et al., 2007)



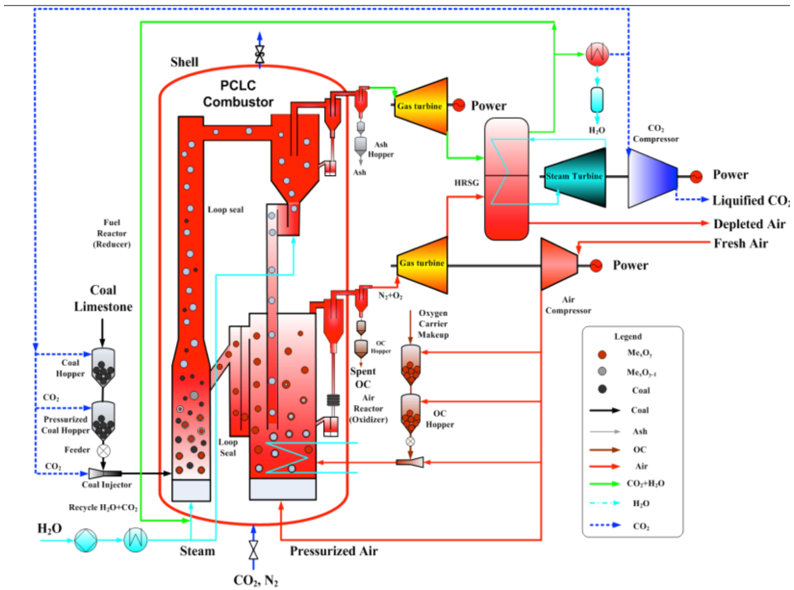
Two Loop High Density CFB System (Kulah et al., 2008)

Kirbas G, Kim SW, Bi X, Lim J, Grace JR. Radial Distribution of Local Concentration Weighted Particle Velocities in High Density Circulating Fluidized Beds. Paper presented at: The 12th International Conference on Fluidization - New Horizons in Fluidization Engineering; May 13-17, 2007; Vancouver, Canada.

Kulah G, Song X, Bi HT, Lim CJ, Grace JR. A NOVEL SYSTEM FOR MEASURING SOLIDS DISPERSION IN CIRCULATING FLUIDIZED BEDS. Paper presented at: 9th International Conference on Circulating Fluidized Beds; May, 13 – 16, 2008; Hamburg, Germany.

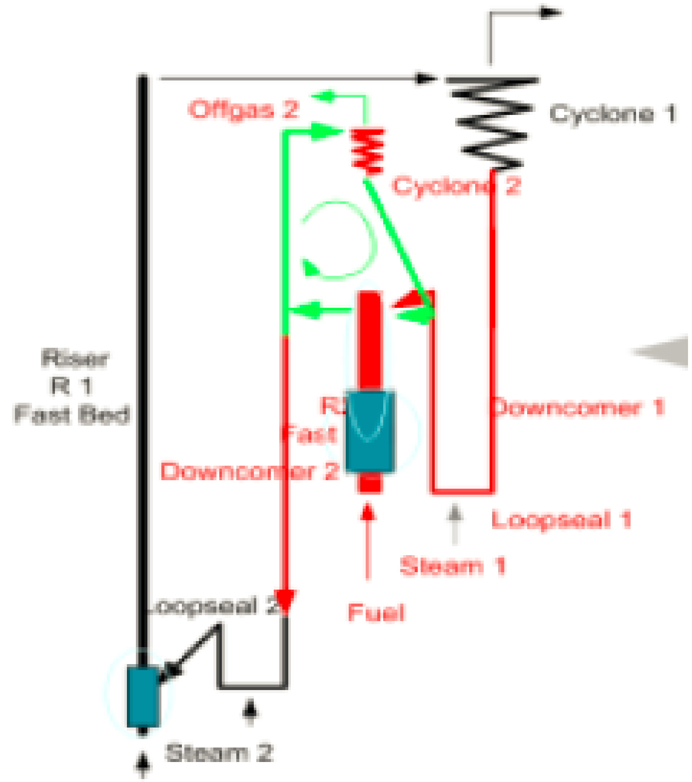
Mode 1 Fluidized Bed Reducer Processes

Southeast Univ. PCLC



- Interconnected bubbling fluidized bed reducer and combustor
- OC: iron ore
- 19 hours of operation with coal
- Coal Feed: bituminous 7 kg/hr (~50 kW_{th})

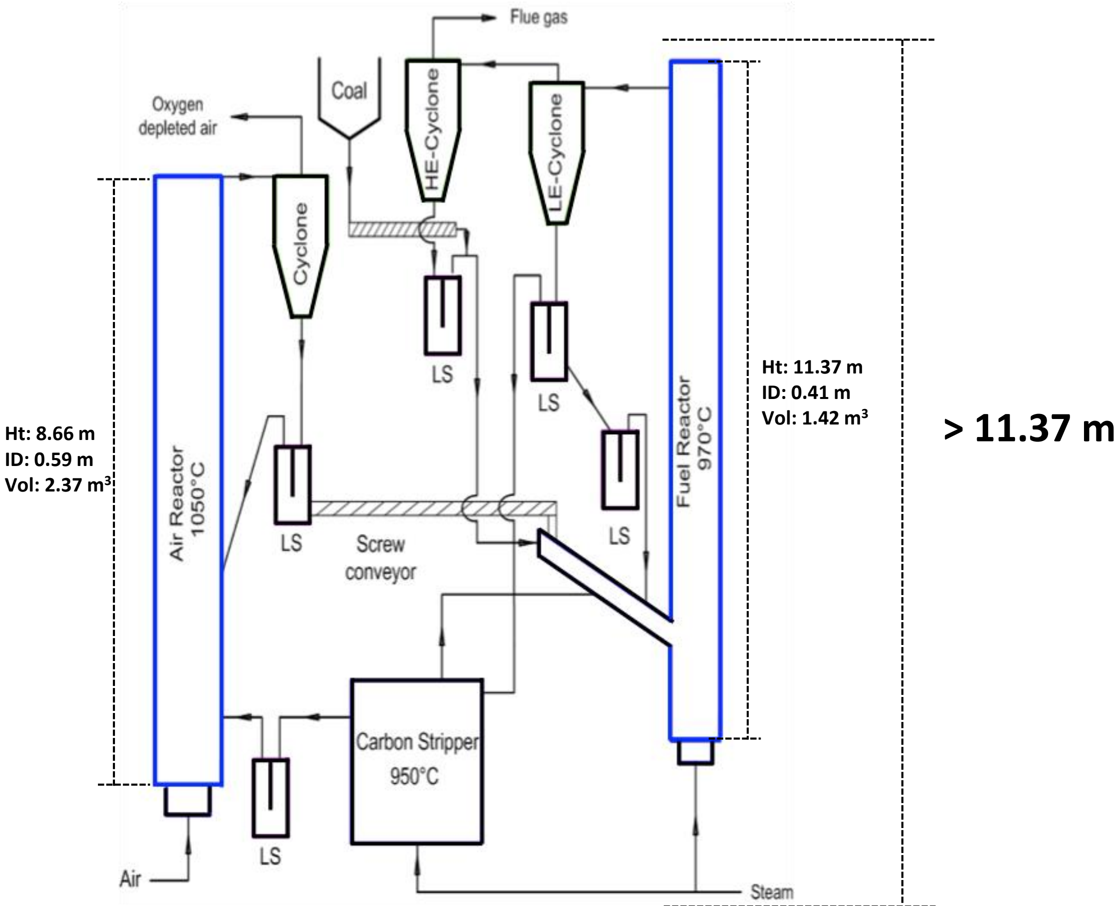
WKU – 10 kW_{th}



- Interconnected fluidized bed
- OC: Cu-based synthesized OC
- 10-hour operations
- Fuels Test: bitumen, asphalt, methane, syngas – no coal tests reported

1 MW_{th} Chemical Looping Combustion Pilot Unit

Alstom – Darmstadt MeO_x[1]



Total Reactor Volume: 3.80 m^3

- Mechanical solid conveying
- Carbon stripper required
- Multiple components – difficult to integrate

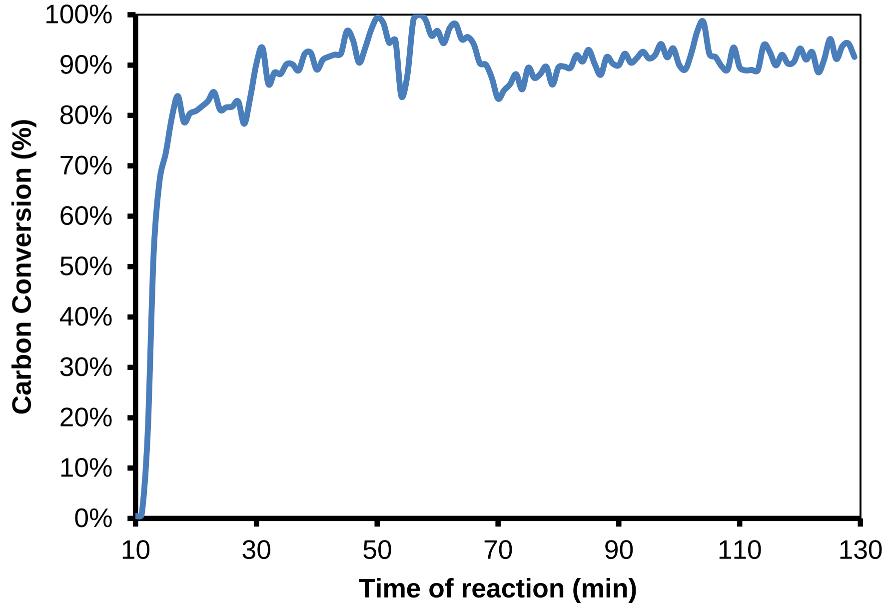
1. Abdulally, I. et al. Clearwater Clean Coal & Fuel Conference 2012 43–54.

25 kW_{th} OSU Sub-Pilot CDCL Process for Coal Combustion

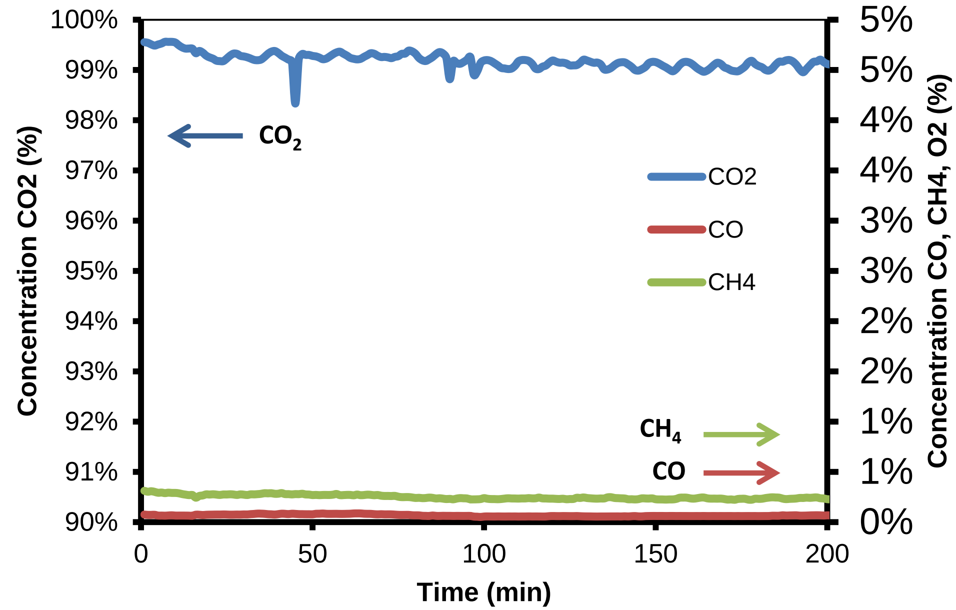
- Fully assembled and operational
- 500+ hours of operational experience
- 200+ hours continuous successful operation
- Smooth solid circulation
- Confirmed non-mechanical gas sealing under reactive conditions
- 13 test campaigns completed

200+ Hour Sub-Pilot Continuous Run - *Sample Results*

Once-Through Reducer Carbon Conversion Profile

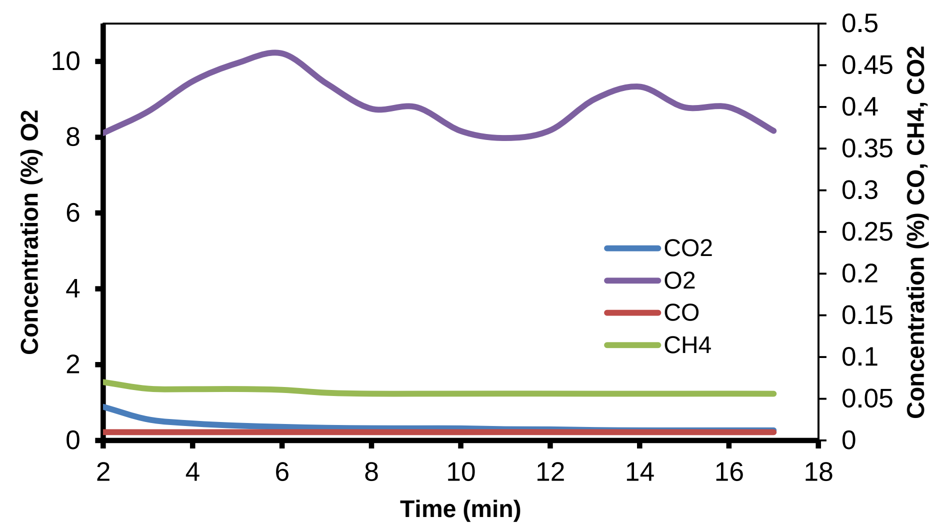


Reducer Gas Concentration Profile



- **Continuous steady >90% carbon conversion from reducer throughout all solid fuel loading (5- 25kW_{th})**
- **<0.25% CO and CH_4 in reducer outlet = full fuel conversion to CO_2/H_2O**
- **<0.1% CO, CO_2, and CH_4 in combustor = negligible carbon carry over, nearly 100% carbon capture**

Combustor Gas Concentration Profile



CDCL NO_x/SO_x Analysis

	Reducer	Combustor
SO_x (ppm)	190-1170	0 - 70
NO_x (lb/MMBTU)	0.100 – 0.200*	~ 0

*Conventional PC Boiler NO_x Generation = 0.2 – 0.5 lb/MMBTU[1]

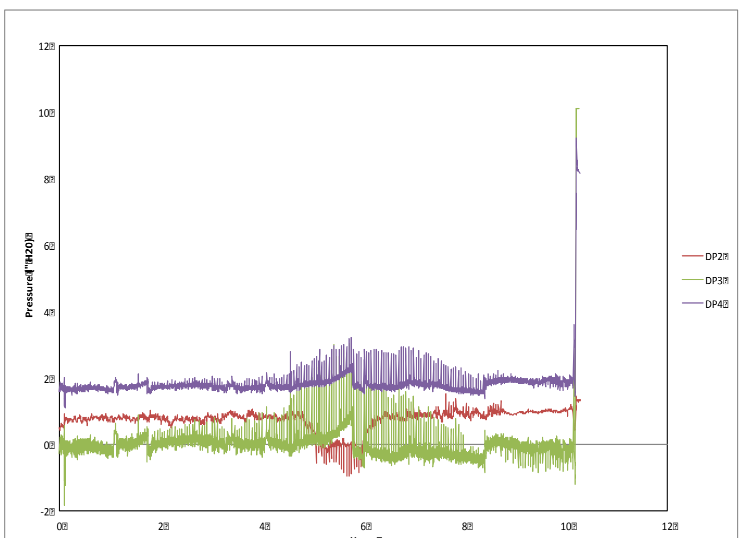
1. NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 1 & 3b

25 kW_{th} OSU Sub-Pilot SCL Process for Hydrogen Generation

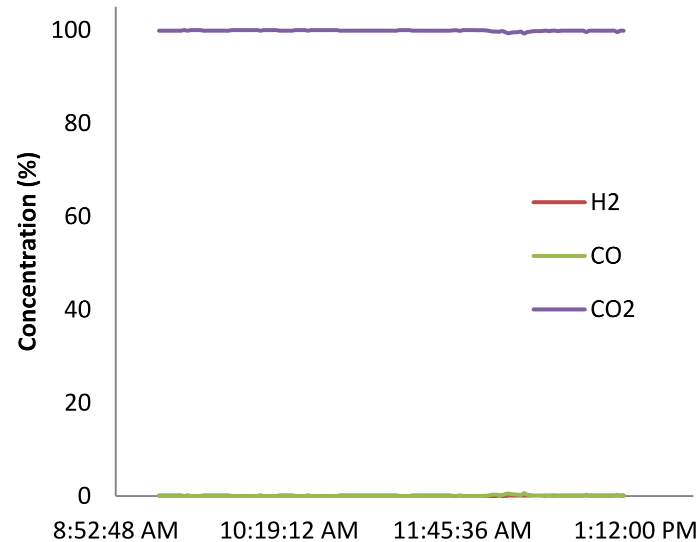
Recent Unit Demonstration

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

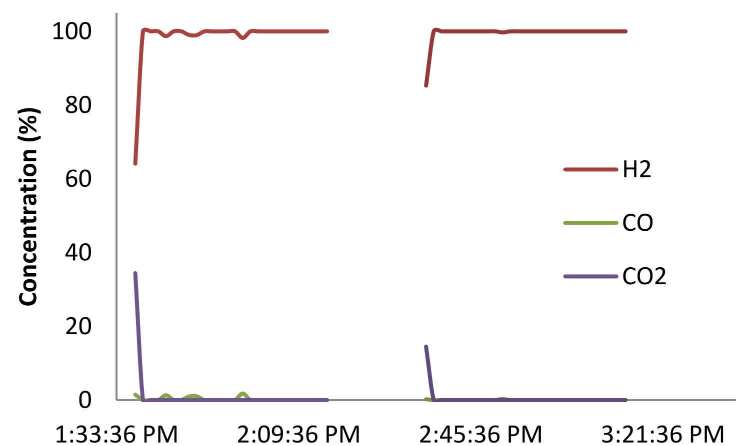
Differential Pressure Profile



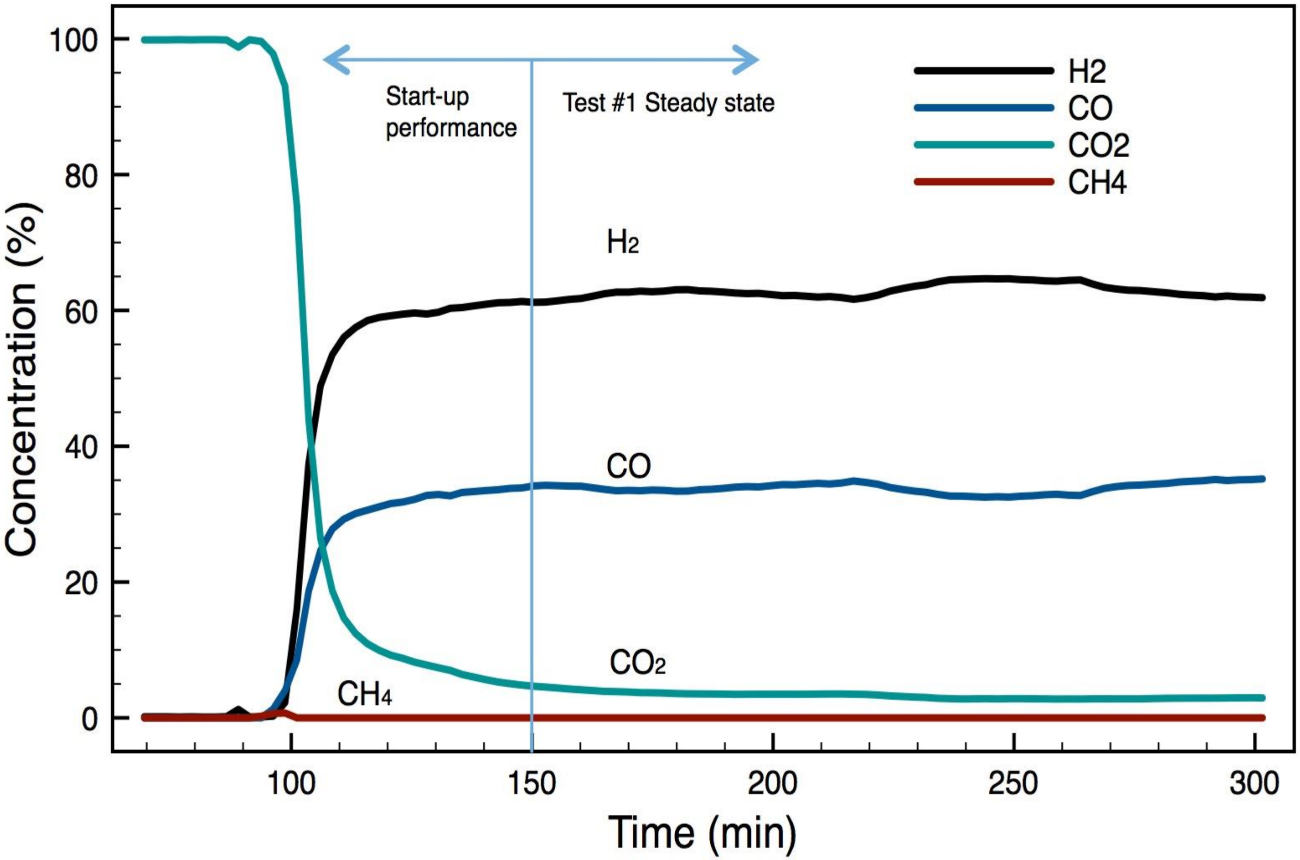
Reducer Gas Composition



Oxidizer Gas Composition



Shale-Gas to Syngas (STS) Sub-Pilot Plant Data



- **100% Methane Conversion**
- **90% Syngas Purity**
- **2:1 Ratio**
  - **Suitable for Liquid Fuel Synthesis**

Concluding Remarks

- **Chemical Looping embodies all elements of particle science and technology - particle synthesis, reactivity and mechanical properties, flow stability and contact mechanics, gas-solid reaction engineering…**
- **OSU processes characterized by the moving bed reducer configuration are compact in design and high efficiency in operation. Success achieved in the operation of 200+ hour continuous sub-pilot CDCL run using coal and progress made in the on-going SYNGAS Chemical Looping pilot demonstration reflect the likelihood of commercialization of these technologies in the near future.**

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