DOE-ARRA Geologic Sequestration Training and Research 2011 Yearly Review Meeting

Project DE-FE0001808

Novel Oxygen Carriers For Coal-Fueled Chemical Looping Combustion

Western Kentucky University

Presenter: Dr. Yan Cao

Institute for Combustion Science and Environmental Technology

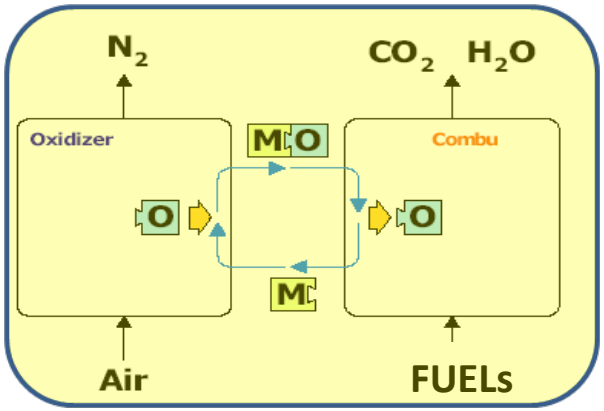
February 25, 2011

Project Participants

- PIs: Dr. Wei-Ping Pan
  Dr. Yan Cao
- Students: Ms. Wen Ying (Master student)
  Mr. Andy Wang (Undergraduate student)
  Mr. Yanwen Cui (Master student)

Introduction (limit - 1 slide)

- Background on the project



Chemical Looping Combustion

→ **Solid Oxygen Carriers**

- Anticipated benefits

1. Commercially accepted kinetics – coupling and potential uncoupling (free oxygen)
2. Thermal Stability, Lower degradation, and Lower Attrition loss
3. Favored thermodynamics for pure CO_2
4. Opportunity to release of free oxygen for improvement of process kinetics;
5. Environmentally sound
6. Economic

Project Objectives (limit – 1 slide)

- Major Objective
  1. Develop a series of advanced oxygen carriers for coal-fueled chemical looping combustion;
  2. Improve the oxygen-transfer capability;
  3. Generate high purity of CO_2;
  4. Increase the reactivity, attrition-resistance and thermal stability in redox cycles;
  5. Achieve an auto-thermal heat balance;
- Secondary Objectives
  1. Achieve 864-cycles (total 3-day (72 hours), residence time=5min/cycle) in TG using gas fuels
  2. Achieve the initial operation of selected oxygen carriers in a 10 kW hot-model chemical looping combustion facility using gas fuels
  3. Achieve multiply 20 cycles in a 100 W continuous fluidized bed using coal as fuel

Project Funding

- Total Project Cost: $ 300,000
- DOE Share: $ 300,000
- Non-DOE Cost Share: none

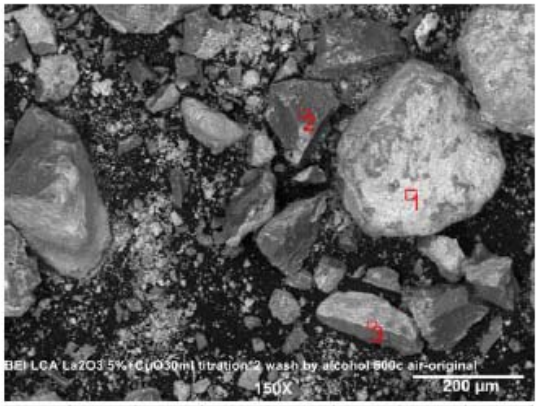
Highlights of Project to Date

- Accomplished 300-cycles run of the 1st prepared oxygen carrier sample (the residence time=5min/cycle) in TG using gas fuels
- Accomplished the 1st oxygen carrier sample in a 10 kW CLC facility using gas fuel (the accumulated time of 50 hours) using gas fuel
- Accomplished 20 cycles of the 1st oxygen carrier in a 100 W continuous fluidized bed using coal as fuel
- Full setup of evaluation platform, including cold-model CLC facility, 100 W bench-scale and continuous-in/out fluidized bed CLC facility and 10 kW CLC facility
- Full setup of oxygen carrier sample characterization tools
- Trained Ms students working on all aspects of CLC tests (Basic energy analysis of CO_2 capture, Preparation and Evaluation of oxygen carrier, Handling of Instrument and testing facility)

Highlights of Project to Date

Figure 1. SEM-EDS analysis of CLCA samples before and after TPR-TPO tests

Original CLCA samples

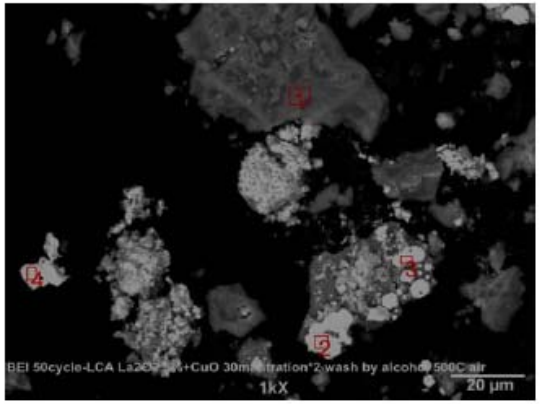


Elt. Point 1	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	35.86	2.187	32.758	12.298	wt.%	
Al	Ka	43.86	2.413	15.02	9.51	wt.%	
Cu	Ka	265.84	5.953	52.045	77.609	wt.%	
La	La	2.99	0.632	0.179	0.582	wt.%	
				100	100	wt.%	Total

Elt. Point 2	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	275.97	6.085	62.446	47.16	wt.%	
Al	Ka	745.85	8.971	34.85	44.13	wt.%	
Cu	Ka	51.6	2.623	2.904	8.71	wt.%	
				100	100	wt.%	Total

Elt. Point 3	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	86.7	3.4	56.6588	30.1538	wt.%	
Al	Ka	91.63	3.495	18.4155	16.5272	wt.%	
Cu	Ka	172.21	4.792	24.674	52.1559	wt.%	
La	La	4.73	0.794	0.25171	1.16317	wt.%	
				100	100	wt.%	Total

CLCA sample after 50 cycles (Scheme 1)

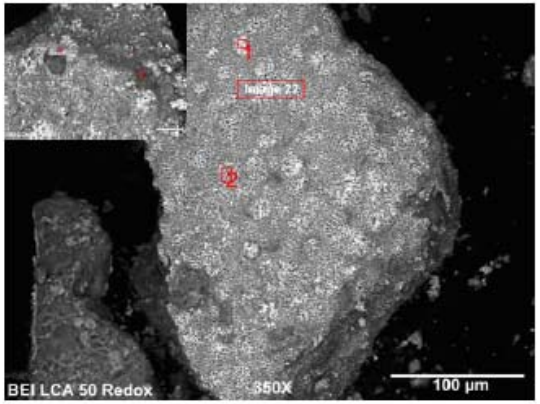


Elt. Point 1	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	42.39	2.377	31.929	12.731	wt.%	
Al	Ka	108.51	3.803	22.806	15.335	wt.%	
Cu	Ka	332.18	6.654	45.129	71.469	wt.%	
La	La	3.01	0.634	0.134	0.467	wt.%	
				100	100	wt.%	Total

Elt. Point 2	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	50.1	2.584	39.692	18.875	wt.%	
Al	Ka	182.54	4.933	30.626	24.560	wt.%	
Cu	Ka	227.5	5.507	29.455	55.629	wt.%	
La	La	4.6	0.783	0.227	0.937	wt.%	
				100	100	wt.%	Total

Elt. Point 3	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	260.78	5.896	66.873	51.727	wt.%	
Al	Ka	745.75	9.97	30.709	40.059	wt.%	
Cu	Ka	43.38	2.404	2.200	6.761	wt.%	
La	La	7.57	1.005	0.217	1.462	wt.%	
				100	100	wt.%	Total

CLCA sample after 50 cycles (Scheme 2)



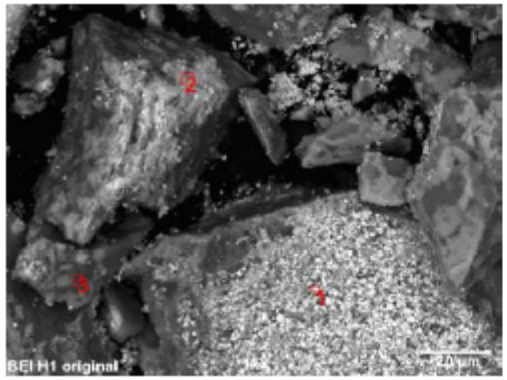
Elt. Point 1	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	28.66	1.955	24.460	14.118	wt.%	
Al	Ka	117.87	3.964	25.549	24.868	wt.%	
Cu	Ka	170.88	4.772	26.351	60.406	wt.%	
La	La	2.13	0.533	0.121	0.608	wt.%	
				100.000	100.000	wt.%	Total

Elt. Point 2	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	18.86	1.586	18.694	10.013	wt.%	
Al	Ka	87.15	3.409	23.148	20.909	wt.%	
Cu	Ka	180.22	4.902	31.902	67.921	wt.%	
La	La	4.14	0.743	0.261	1.147	wt.%	
				100.000	100.000	wt.%	Total

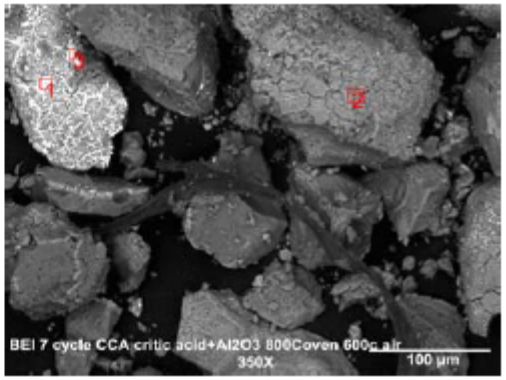
Highlights of Project to Date

Figure 2. SEM images of prepared oxygen carrier samples before and after TPR-TPO tests

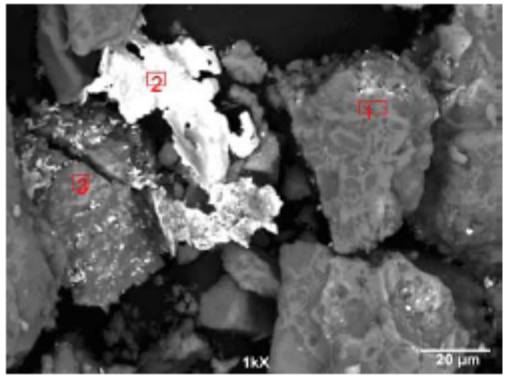
Original CA samples



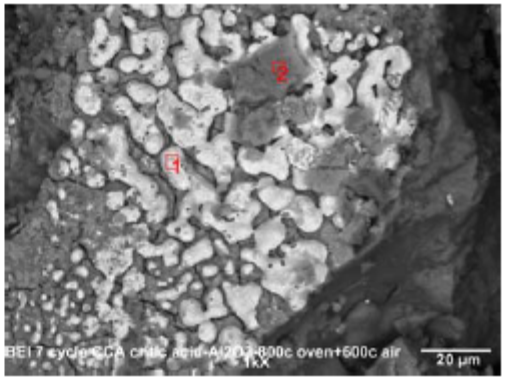
Original CCA samples



CA sample after 20 TPR-TPO cycles



CCA sample after 10 TPR-TPO cycles

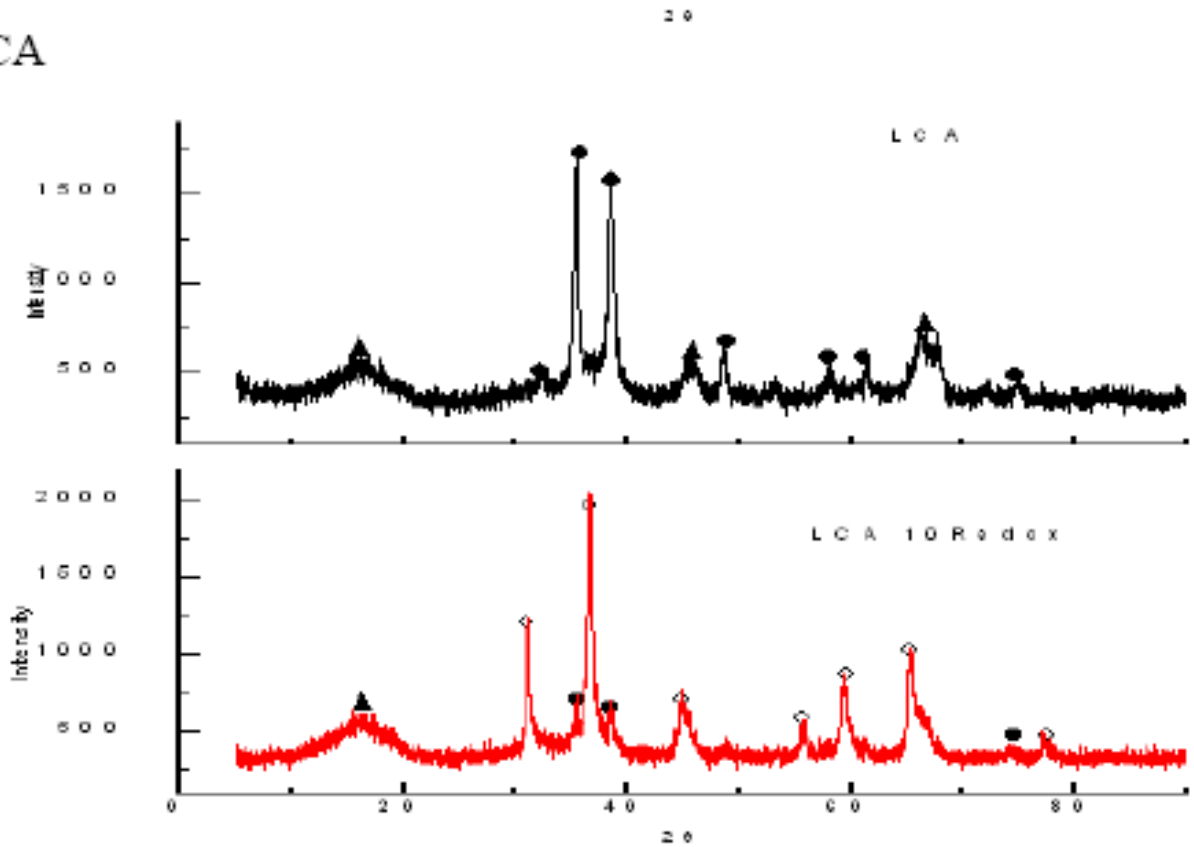


Highlights of Project to Date

Figure 3. XRD analysis oxygen carrier samples after tests

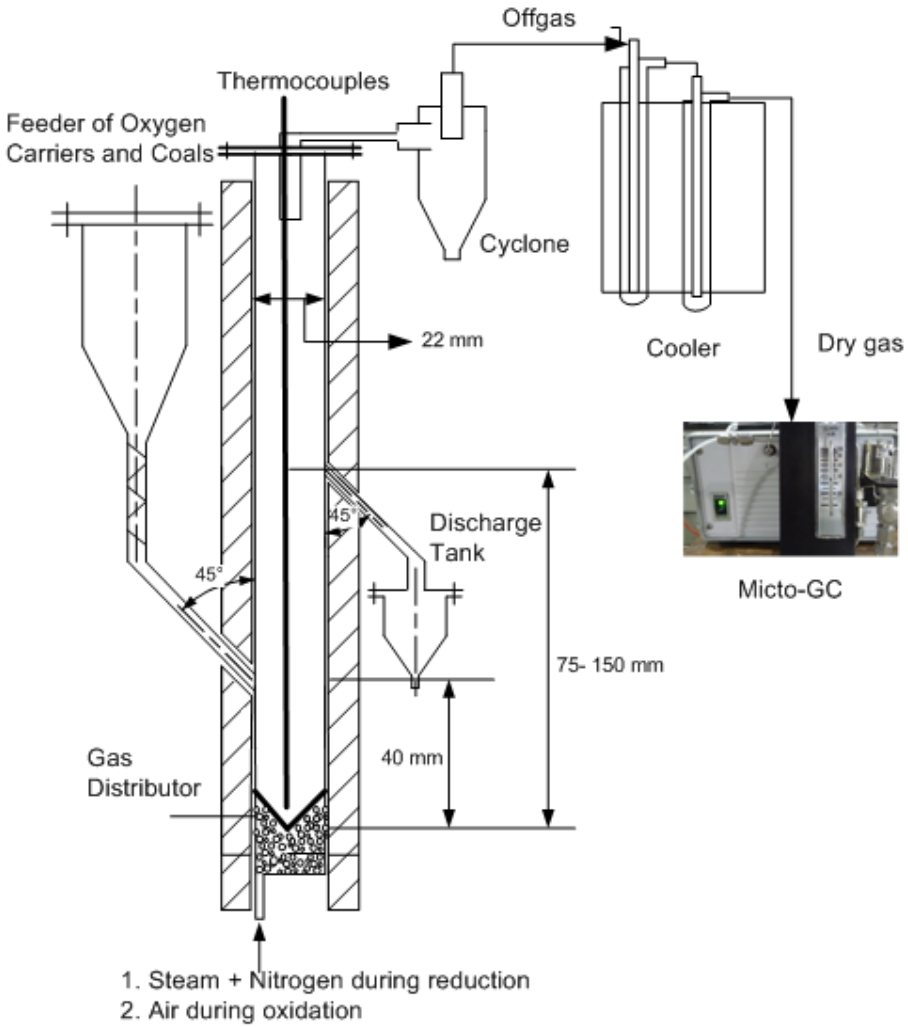
(● CuO; ▲Al2O3; ○ CuAl2O4; Cu2O; ▼CuAlO2; ◎Cu)

Sample CLCA



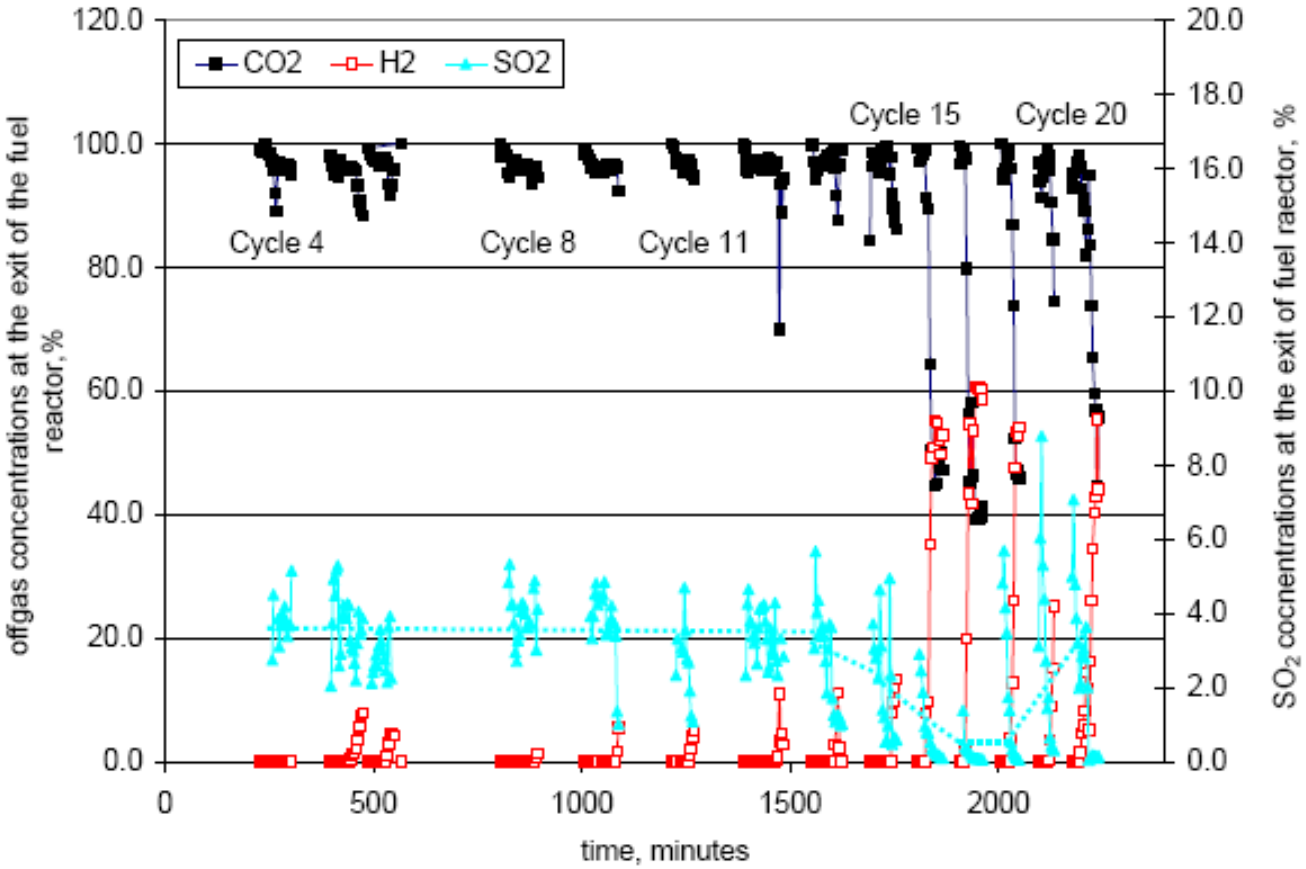
Highlights of Project to Date

Figure 4 Schematic of lab-scale test facility on chemical looping combustion



Highlights of Project to Date

Figure 5. Profiles of gas concentrations at the exit of fuel reactor



Highlights of Project to Date

Figure 6-1. Crystal analysis of fresh and used oxygen carrier samples (CLCA)

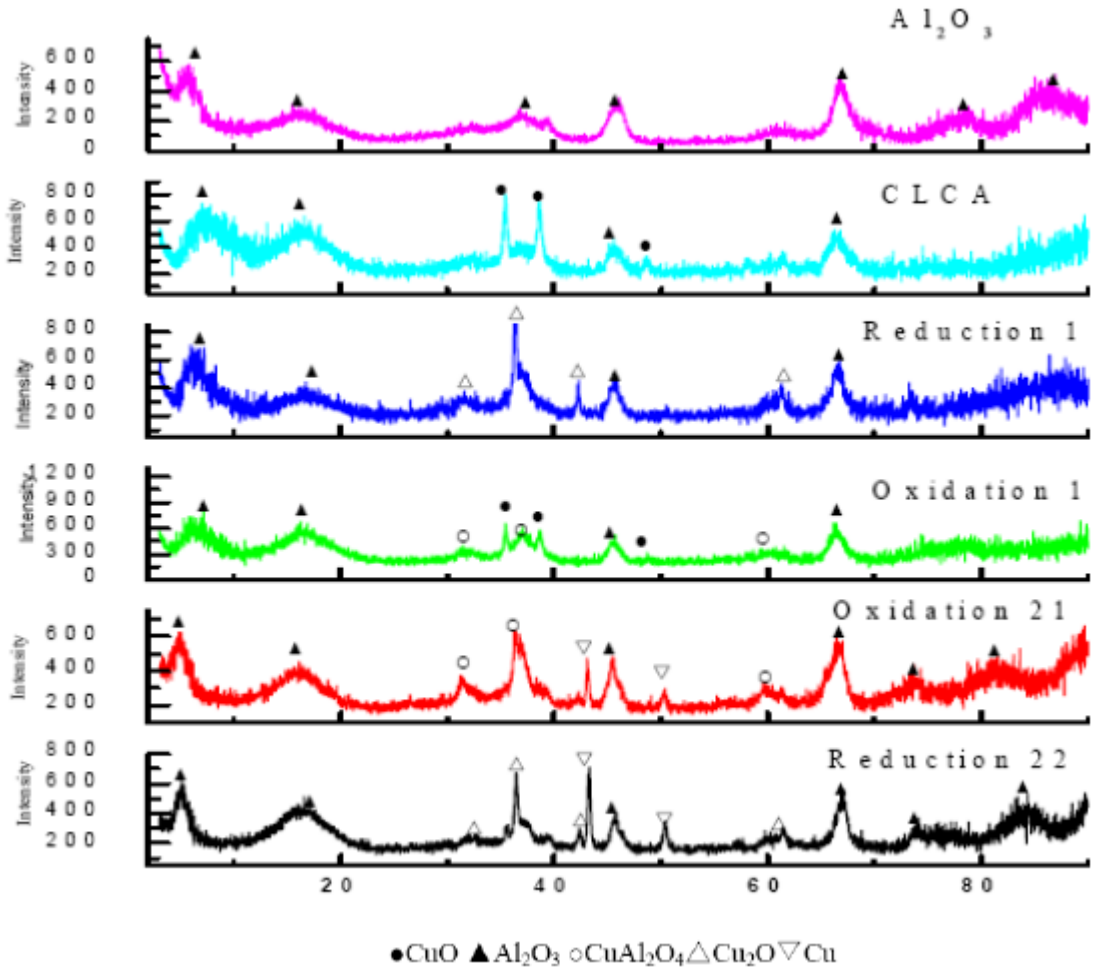
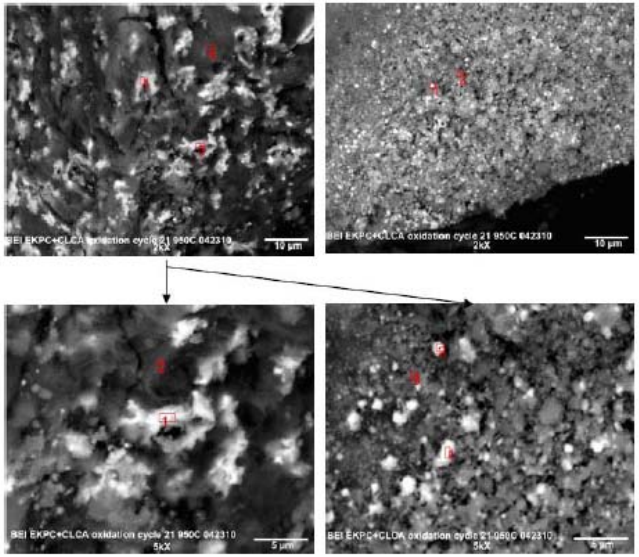


Figure 6-2. SEM pictures of performance-improved oxygen carriers CACA (after 20 cycles operation)

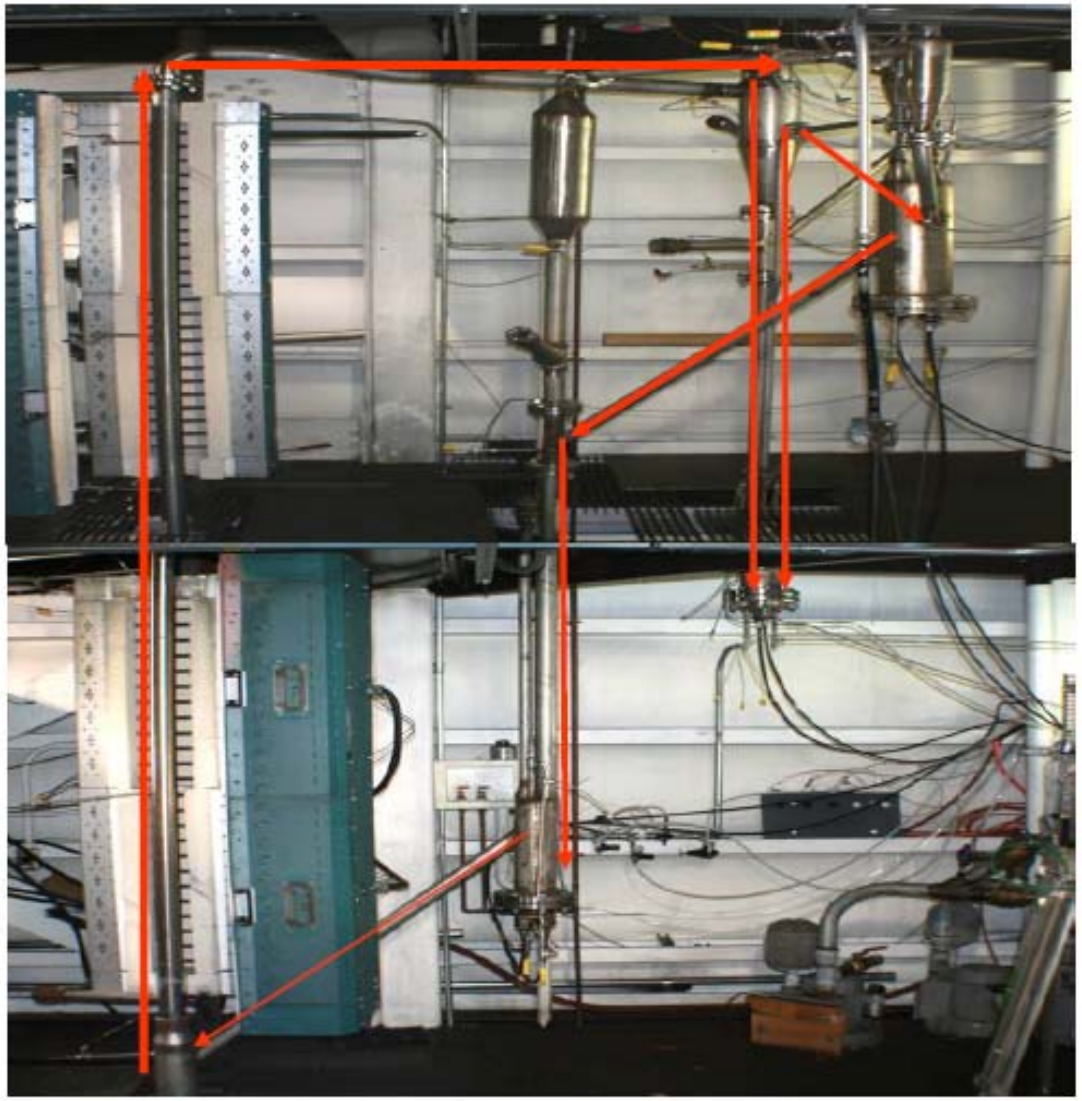


Highlights of Project to Date

Figure 7. 10 kW Cold-model CLC facility

Highlights of Project to Date

Figure 8. 10 kW CLC facility



Tasks – Overview

Task No.	Task Description	Task Duration	Task Funding
1	Project Management and Planning	12/01/2009 – 11/30/2012	$ 25,000
2	**Preparation of Oxygen Carriers**	12/01/2009 – 12/25/2011	$ 125,000
3	**Improvement of Chemical Formula of Oxygen Carriers, Finalization of Oxygen Carriers**	12/01/2009 – 6/30/2012	$ 125,000
4	**Evaluation of Oxygen Carriers in a Cyclic TGA Operation**	12/01/2010 – 12/30/2011	$ 250,000
5	**Conducting 10kW Model CLC Testing with Oxygen Carriers using gas Fuels**	12/01/2012 – 3/30/2012	$ 200,000
6	**Conducting 100W Model CLC Testing with Oxygen Carriers using Coals**	7/01/2009 – 12/30/2011	$ 150,000

Project Schedule

Year		2010				2011				2012			
Quarter		1	2	3	4	1	2	3	4	1	2	3	4
Task 1.0	Project Management and Planning												
Subtask 1.1	Project Management Plan												
Subtask 1.2	Project Management												
Task 2.0	Preparation of Oxygen Carriers												
Subtask 2.1	Development of Category 1 Oxygen Carriers												
Subtask 2.2	Development of Category 2 Oxygen carriers												
Subtask 2.3	Development of Category 3 Oxygen Carriers												
Task 3.0	Selection of Oxygen Carriers												
Subtask 3.1	Improvement of Chemical Formula of Oxygen Carriers												
Subtask 3.2	Finalization of Oxygen Carriers												
Task 4.0	Evaluation of Oxygen Carriers in a 10 kW Hot-model CLC Facility												
Subtask 4.1	Modification of a 10 kW Hot-model CLC Facility												
Subtask 4.2	Conducting 10 kW Model CLC Testing with Oxygen Carriers												

Discussion

Major issues/problems (if applicable)

- Supporting material: γ-Al_2O_3 (higher cost, wasted larger surface area and pore volume, thermal-unstable)
  1. Solution1 (the 2nd oxygen carrier): clay material (cheaper, minimal amounts of impurities decreasing thermal-stability and sulfur retention and transfer to air reactor) (100 % complete)
  2. Solution 2 (the 2nd oxygen carrier): α-Al_2O_3 (lower cost, thermally-stable, optimized pore volume usage (60 % complete)
  3. Solution 3 (the 3rd oxygen carrier): bulk-mixing and hydro-thermal preparation of CuO and α-Al_2O_3 powders (20 % complete)

Discussion

Major issues/problems (if applicable)

- Coupling and Uncoupling

  1. Coupling CLC (50 % complete)

     enhancing material for the prevention of thermally-melting reduced copper, accomplished the initial formula and trying the 2nd formula

  2. Uncoupling CLC (50 % complete)

     kinetics of free oxygen release

     measurement of free oxygen

Discussion

Major issues/problems (if applicable)

- 10 kW CLC facility And Sample Evaluation

  1. Cold-model CLC (75 % complete)

     flow dynamics – successful smooth operation of the dual-fluidized bed CLC facility

  2. Hot-model CLC (40 % complete)

     Current status: 3 kW CLC operation

     optimization of 10 kW CLC system setup and operation is on-going

Project Milestones

(Include HQ and project milestones)

Milestone	Planned Completion Date	Actual Completion Date
The 1st successful oxygen carrier sample	12/31/2010	12/31/2010
The 2nd successful oxygen carrier sample	06/30/2011	03/30/2011
The 3rd successful oxygen carrier sample	03/30/2012	
10kW CH_4-firing CLC operation using the 1st oxygen carrier sample	06/30.2011	Preliminary test-11/30/2010
100 W fluidized bed cyclic operation	2012	2011 (20 cycles)

Anticipated Efforts for the Coming Year

- The 1st Oxygen Carrier Sample will be evaluated in the 10 kW CLC operation of over 6-8 hours
- The 2nd and 3rd Oxygen Carriers will be prepared, and their multi-performance was evaluated using TG and 100 W fluidized bed
- All samples will be characterized using XRD, BET, SEM and Chemi-Sorp
- Optimization of sample formula will be continuously conducted
- Etc

PI Contact Information

- If you have any questions or would be interested in collaboration please contact

wei-ping.pan@wku.edu

yan.cao@wku.edu