



Scale-up of Chemical Looping Reactors: Practical Considerations and Design of Industrial Systems

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5th International Chemical Looping Conference
Park City, Utah

9/25/2018

Acknowledgments

Babcock & Wilcox

- Jinhua Bao
- Barteve Sakadjian
- Prasanna Seshadri
- Luis Velazquez-Vargas

Clearskies Consulting

- Robert Statnick

Dover Light & Power

- Dave Filippi

Electric Power Research Institute

- Andrew Maxson

Industrial Review Committee

- AEP, CONSOL, DOE, Duke Energy, First Energy, Ohio Development Services Agency, Tri-States

Johnson-Matthey

- Gareth Williams
- Andrew Scullard

Ohio State University

- L-S Fan
- Andrew Tong
- Dawei Wang

Trinity Consulting

- Mike Burr
- Dave Stroh

WorleyParsons

- Jim Simpson
- Xie Qinghua

Overview

► Purpose

- Bench-scale and pilot-scale demonstrations have significantly advanced chemical looping technology
- Intermediate-scale demonstrations must bridge technology gap and incorporate features of commercial-scale units
- Active applications of chemical looping applications growing

► Goal of Presentation

- Provide non-technology specific discussion of scale-up considerations and design issues.
- Focus on power as most complicated implementation

► Objectives

- Particle manufacture
- Reactor scale-up
- Thermal integration
- Environmental
- Sparing philosophy
- Operation
- Safety

Particle Manufacture Scale-up

Particle formulation and performance demonstrated successfully at small scale

Raw material sourcing & specification

Material(s) processing issues:

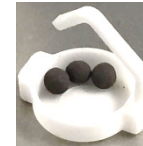
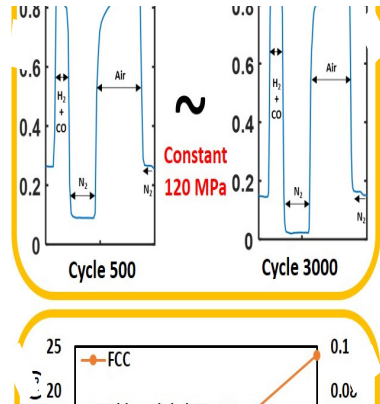
- Flowability and segregation
- Hygroscopicity and compactability
- Gel/emulsion/suspension stability

Equipment scale-up issues:

- Intermediate stages required
- Mixing and comminution effectiveness and energy demand
- Heating/cooling kinetics
- Temperature uniformity
- Safety risk assessments / hazard studies

Control issues:

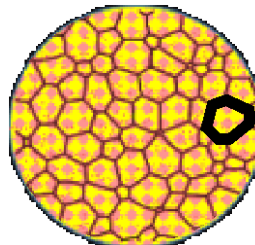
- Process monitoring and control
- Product specifications
- Process cost evaluation



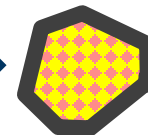
After 0 redox cycles



After 3,000 redox cycles

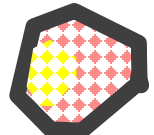


Partially Isolated Particle



Before Redox

Confined Particle Evolution

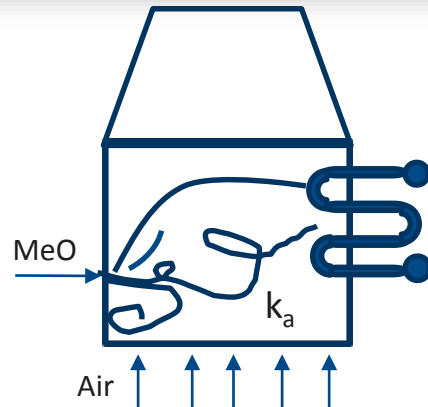


After Redox



Reactor Scale-up

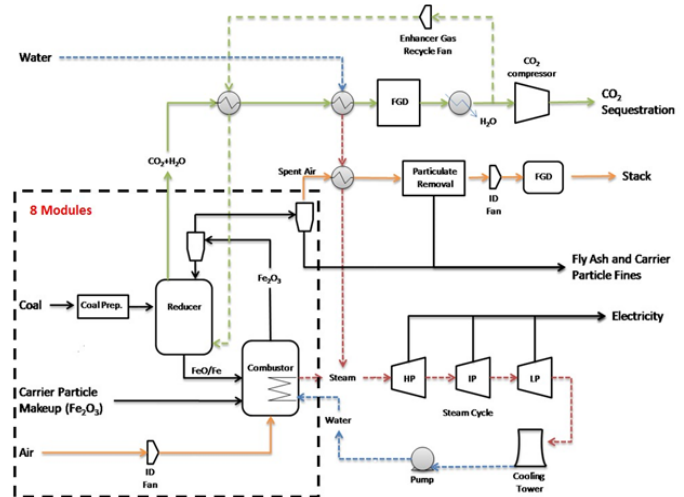
- ▶ **Surface-to-volume ratio**
 - Refractory-lined, electrically heated
 - Membrane wall
- ▶ **Feed point spacing – unit cell**
 - Fuel
 - Metal Oxide
- ▶ **Matching air/fuel distribution and kinetics to lateral and vertical mixing rates**
 - Multiphase computational fluid dynamic models (MFiX, Barracuda® and Fluent) provide effective design tool
 - Intrinsic kinetic and mixing data from laboratory and sub-pilot facilities



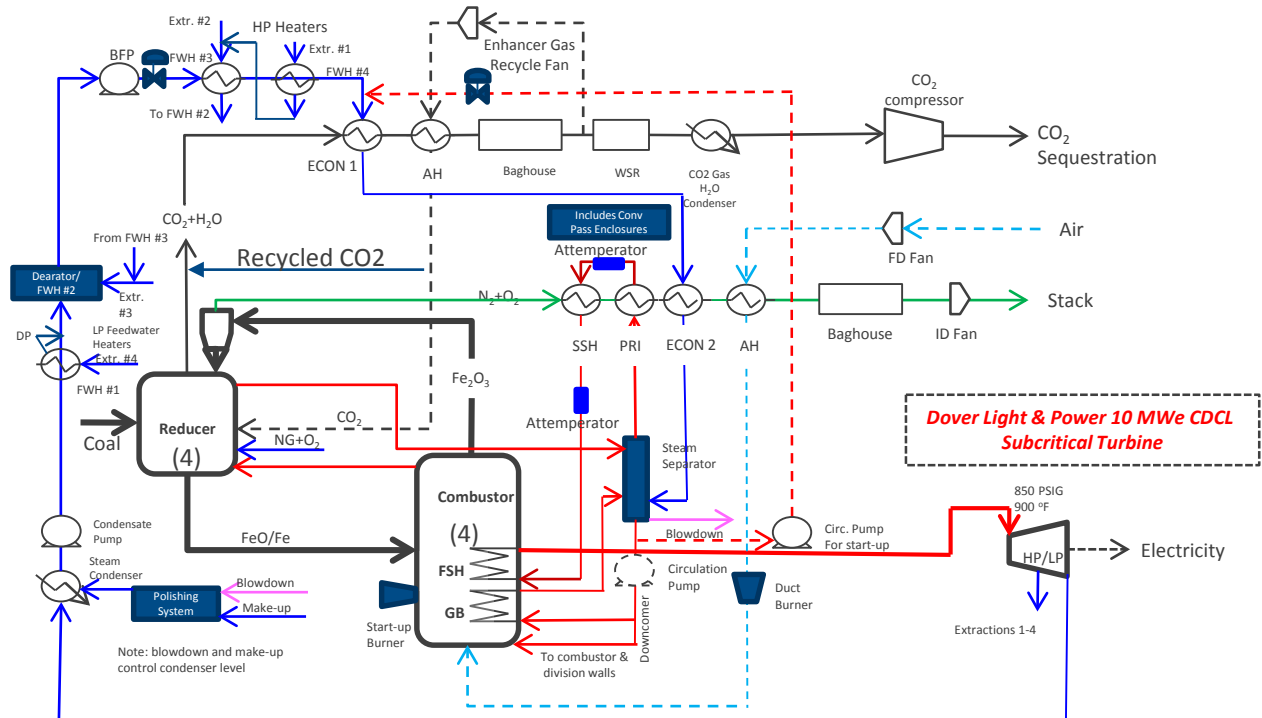
Thermal Integration – High-Grade Heat Recovery

► Steam Cycle

- Heat recovery schemes
 - Pinch analysis - ASPEN Energy Analyzer module
- Metal temperatures
 - Sufficient cooling during start-up or part-load
 - Gas tempering with recycle
 - Attemperator sprays
- Steam separation (subcritical) or once-through design (supercritical)
- High temperature valves

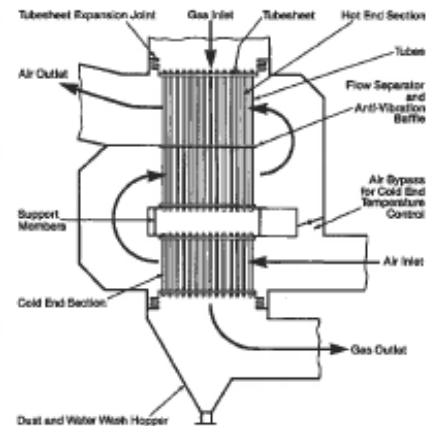
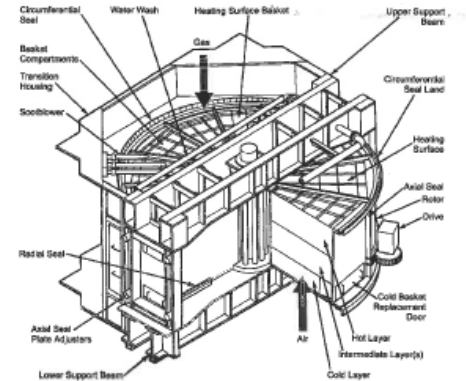


Thermal Integration



Thermal Integration – Low-Grade Heat Recovery

- ▶ **Mismatch between reducer and combustor exhaust gas**
- ▶ **Air Heaters**
 - Coal dryer
 - Pulverizer
- ▶ **Air heater for combustion air – regenerative design**
- ▶ **Gas heater for recycle CO₂ – tubular design???**



Steam: its generation and use edition 41, The Babcock & Wilcox Company, 2005.

Environmental

► Split backpass issues

- CO₂ for baghouse cleaning – pulse jet or reverse flow – not chemical looping specific
- Strict emission limits for pipeline quality CO₂
- Wet scrubber performance with CO₂-rich flue gas
- SO₂ and H₂S removal

► Permitting

- Pilot facility demonstrated emissions for permit application
- Waste disposal of metal oxide
- CO₂ credits???
 - Sequestration
 - Beneficial use

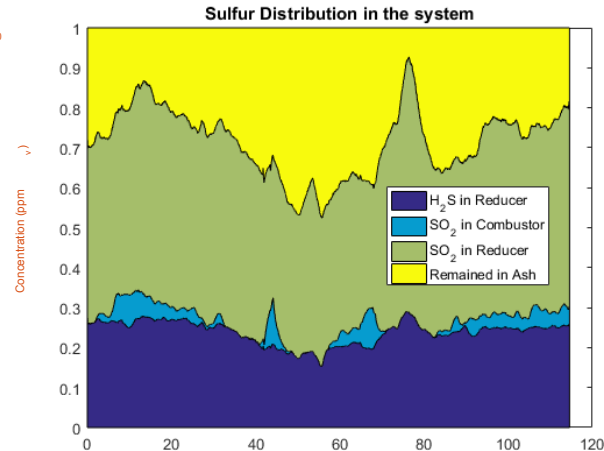
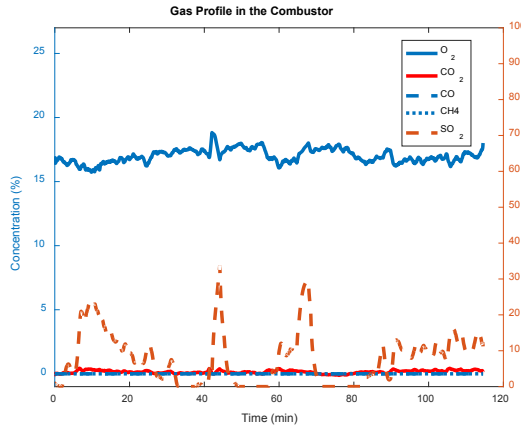
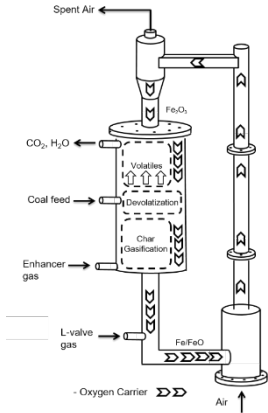
Exhibit 2-1 CO₂ Stream Compositions Recommended Limits

Component	Unit (Max unless Otherwise noted)	Carbon Steel Pipeline		Enhanced Oil Recovery		Saline Reservoir Sequestration		Saline Reservoir CO ₂ & H ₂ S Co-sequestration		Venting Concerns (See Section 3.0)
		Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	
CO ₂	vol% (Min)	95	90-99.8	95	90-99.8	95	90-99.8	95	20 - 99.8	Yes-IDLH 40,000 ppmv
H ₂ O	ppm _w	300	20 - 650	300	20 - 650	300	20 - 650	300	20 - 650	
N ₂	vol%	4	0.01 - 7	1	0.01 - 2	4	0.01 - 7	4	0.01 - 7	
O ₂	vol%	4	0.01 - 4	0.01	0.001 - 1.3	4	0.01 - 4	4	0.01 - 4	
Ar	vol%	4	0.01 - 4	1	0.01 - 1	4	0.01 - 4	4	0.01 - 4	
CH ₄	vol%	4	0.01 - 4	1	0.01 - 2	4	0.01 - 4	4	0.01 - 4	Yes-Asphyxiate, Explosive
H ₂	vol%	4	0.01 - 4	1	0.01 - 1	4	0.01 - 4	4	0.02 - 4	Yes-Asphyxiate, Explosive
CO	ppmv	35	10 - 5000	35	10 - 5000	35	10 - 5000	35	10 - 5000	Yes-IDLH 1,200 ppmv
H ₂ S	vol%	0.01	0.002 - 1.3	0.01	0.002 - 1.3	0.01	0.002 - 1.3	75	10 - 77	Yes-IDLH 100 ppmv
SO ₂	ppmv	100	10 - 50000	100	10 - 50000	100	10 - 50000	100	10 - 50000	Yes-IDLH 100 ppmv
NO _x	ppmv	100	20 - 2500	100	20 - 2500	100	20 - 2500	100	20 - 2500	Yes-IDLH NO-100 ppmv, NO ₂ - 200 ppmv

Source: "QGESS: CO₂ Impurity Design Parameters", NETL August 2013, DOE/NETL-341/011212

Fate of Sulfur: Injection of high sulfur coal

25 kW_{th} Sub-Pilot Test Unit



- >95% sulfur capture efficiency
- 1.2 lb SO₂/MW_{gross} from spent air
- Meet EPA's sulfur regulation for new power plants
- Cost saving in desulfurization unit on the combustor

C	H	N	S	O	Ash
71.80	4.22	1.24	1.27	14.02	7.45

Chung, C., Pottimurthy, Y., Tong, A. Applied Energy Journal, 2017

Sparing Philosophy

▸ Single vs. multiple module capacity

- Standalone plant
- Coupled capacity

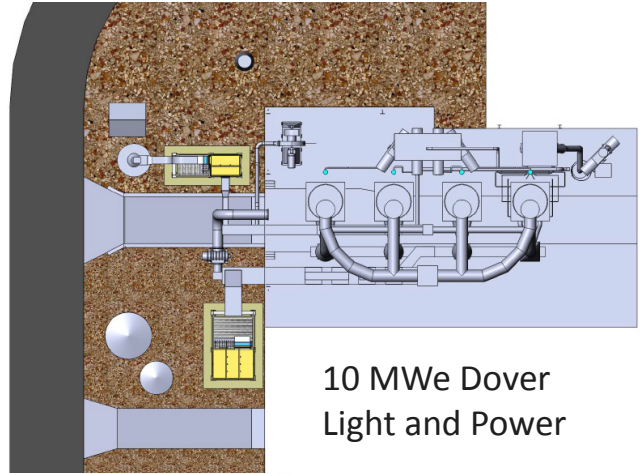
▸ Fuel preparation system capacity

▸ Redundant feedwater and recirculation pumps

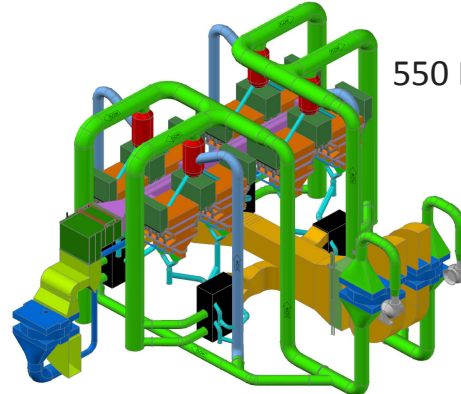
▸ Instrumentation

▸ Environmental equipment

- No redundancy in wet scrubber
- Spare baghouse modules



10 MWe Dover
Light and Power



550 MWe Concept

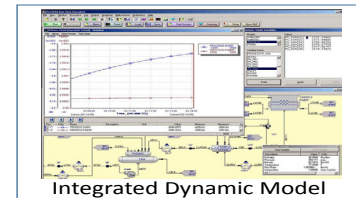
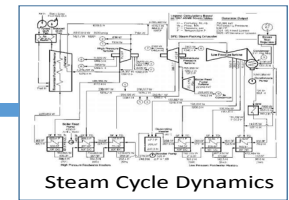
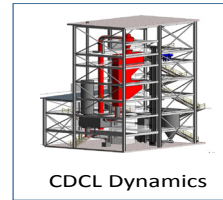
Operation

► Start-up of Modular Reactors

- Start-up burner capacity
- Auxiliary circulation pumps
- Rapid start-up vs baseload

► Transient response

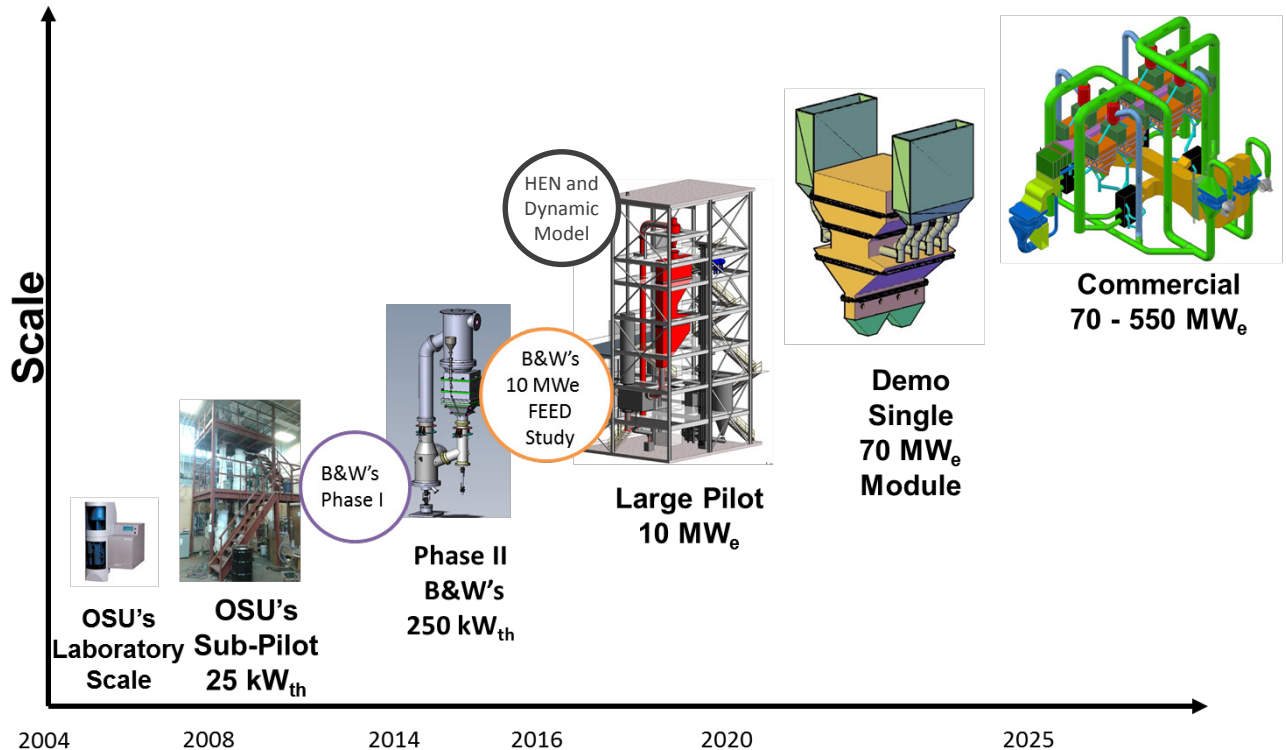
- Long transient response due to inventory of metal oxide (time constants)
- Impact of fuel variability on steam quality
- Shutdown, trip, black plant trip
- ASPEN or ProTRAX dynamic modeling
- Rules-based optimizer or neural net



Safety

- **Hazard Design Analysis and Hazardous Operation Analysis (HAZOP)**
- **Area Classification**
 - Combustible mixtures (Class I Div II Classification)
 - Hydrogen
 - Hydrogen sulfide
- **Pressurized operation for gasification and reforming applications**
- **Metal oxide components**
- **Hazardous waste – exothermic reaction of metal oxide in air**

Commercialization Pathway



Conclusions

- Timing is right to consider scale-up issues.
- Need to consider scale-up in the design of sub-pilot facilities and test conditions – design test matrices that span operating space and provide intrinsic design data.
- Current pilot-scale facilities have many hours of operation but lack thermal integration and heat recovery.
- Start-up, transient operation (e.g., load following), shutdown and black plant trip scenarios introduce additional complexity in the design.
- As a community, success for one is success for all!!!!



Acknowledgments

This presentation is based upon work supported by the Department of Energy under the Awards: [DE-FE0009761](#), [DE-FE0026334](#), [DE-FE0029093](#), [DE-FE0031582](#) and the Ohio Development Services Agency under the Awards: [OER-CDO-D-15-17](#) and [OER-CDO-D-17-03](#).

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