NATIONAL ENERGY TECHNOLOGY LABORATORY

Industrial Carbon Management Initiative (ICMI)

Project Review & Status

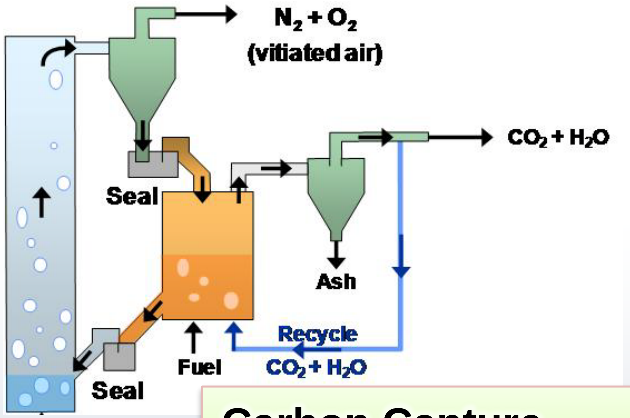
July 2012

Acknowledgements:
…too many names to list…

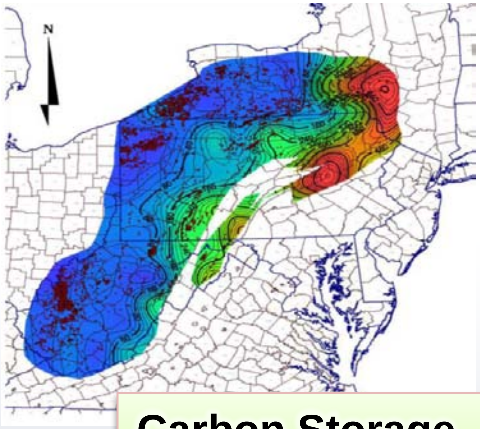
U.S. DEPARTMENT OF ENERGY

ICMI Research areas

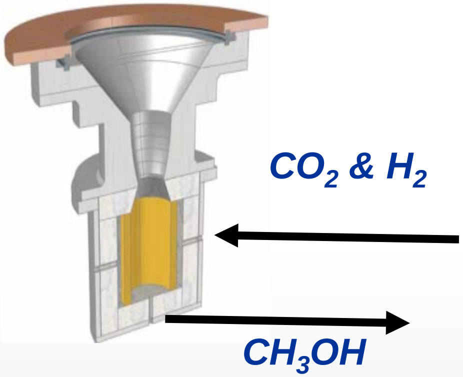
Focus is on "industrial" applications: NG or coal boilers, process heat, chemical production, others. Technical results expected to benefit coal power as well.



Carbon Capture
Chemical Looping Combustion

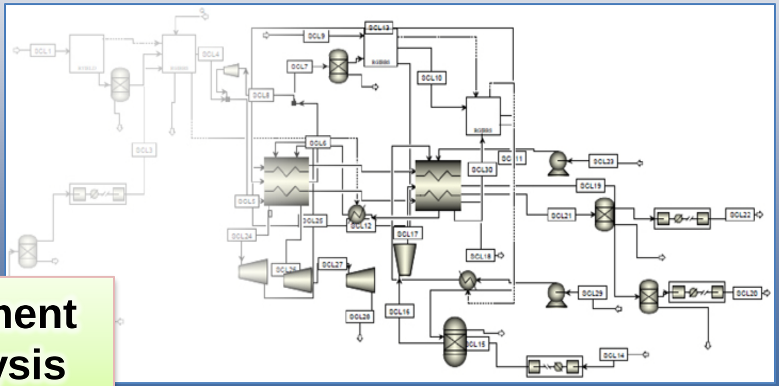


Carbon Storage
Depleted Shale Fields



Carbon Utilization
Photocatalytic Conversion

CCUS for Industrial Applications



Industrial assessment and systems analysis

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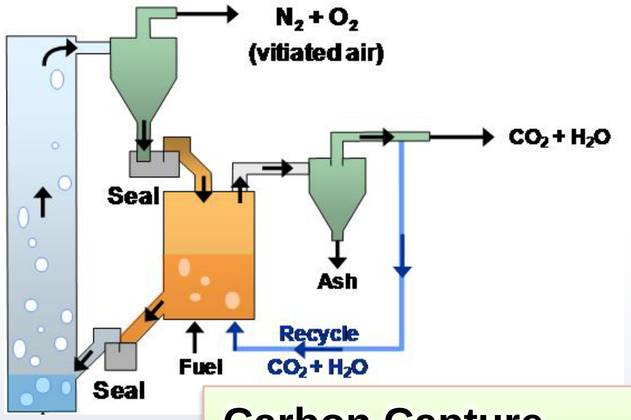
Focus is on "industrial" applications: NG or coal boilers, process heat, chemical production, others.   Technical results expected to benefit coal power as well.



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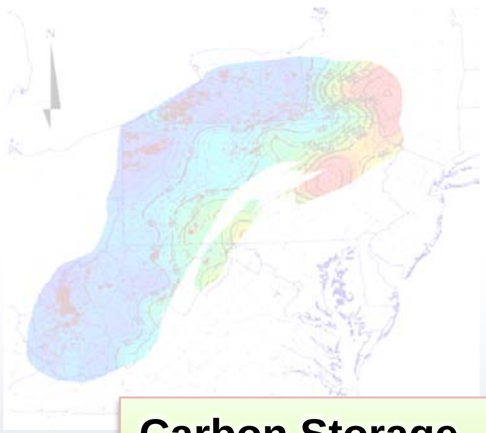

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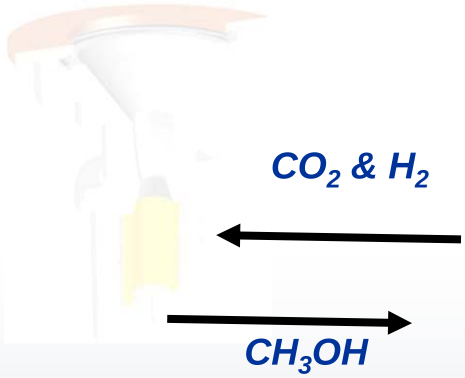

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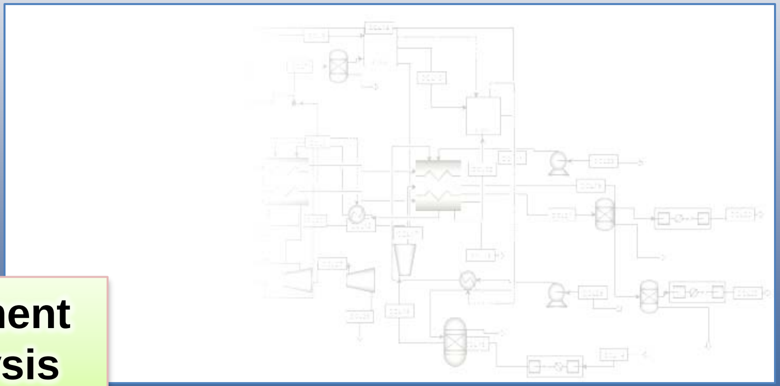
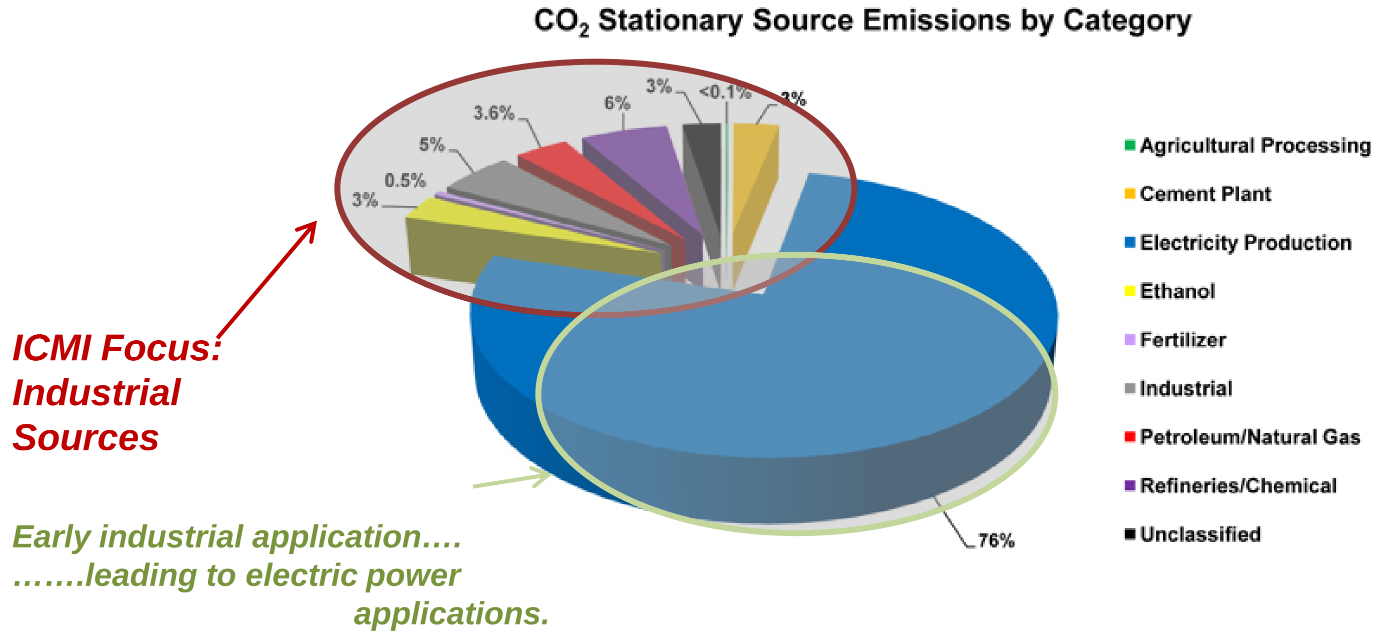


High-potential Industrial Applications

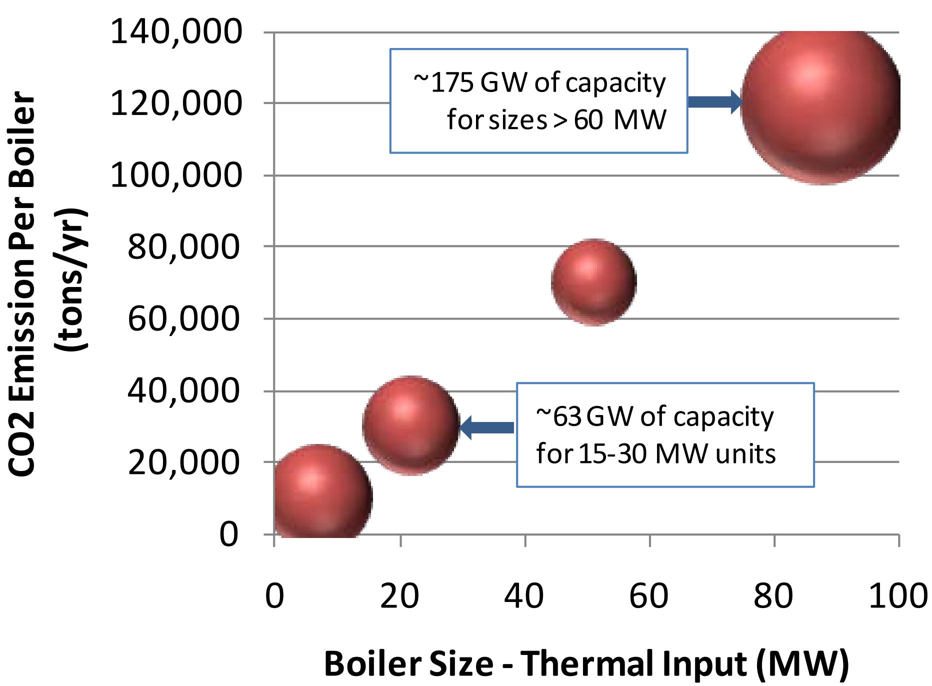
- CL industrial boilers
- CL for oil sands processing and production
- CO_2 sequestration in depleted shale gas reservoirs



Reference for CO_2 Stationary Source Emissions by Category chart:
DOE's Regional Carbon Sequestration Partnerships and NATCARB database.

U.S. Industrial Boiler Market
(Natural Gas)

- **43,000 boilers in the U.S.**
  - More than 50% are smaller than 3 MW_t
- **CO_2 emissions per boiler are comparable to some demonstration CCUS projects, or EOR wells**
- **Old infrastructure**
  - For boilers > 3 MW_t
    - 47% > 40 yrs old
    - 76% > 30 yrs old
  - Expected life 30 yrs
- **NOx requirements**
  - 30-80 ppm @ 3% O_2
  - Larger units are lower



Reference: Booz, Allen, Hamilton, Analysis of Fuel Flexibility Opportunities and Constraints in the U.S. Industrial Sector, Draft Report, March 7, 2007, DOE/EERE

CO_2 Separation Issues for Industrial Boiler Applications

Technology	Issues
Flue-gas scrubbing (e.g. MEA)	• Capital investment for add-on • Chemical handling issues • Need economic cost studies
Membranes	• Low pressure flue gas • Potentially poor energetics • Need economic cost studies
Oxy-fuel	• Capital investment for ASU and exhaust gas recycle • NOx – O_2 purity trade-offs • CO_2 separation is simple • Need economic cost studies
Chemical Looping	• Ultra-low NOx • CO_2 separation is simple • **Need economic cost studies** • **Need to validate technology**

Where and how can chemical looping work?

Industrial applications (includes NG, smaller scale)

Power applications (coal, 100+MW scale)

Attributes:
Fuel (NG, solid fuels)
Size
Cost
Performance

System issues & configuration
Attrition
Material supply & handling
Heat exchanger/integration
Sensors and control
Emissions
Carrier cost/supply & re-use

Components
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Heat transfer
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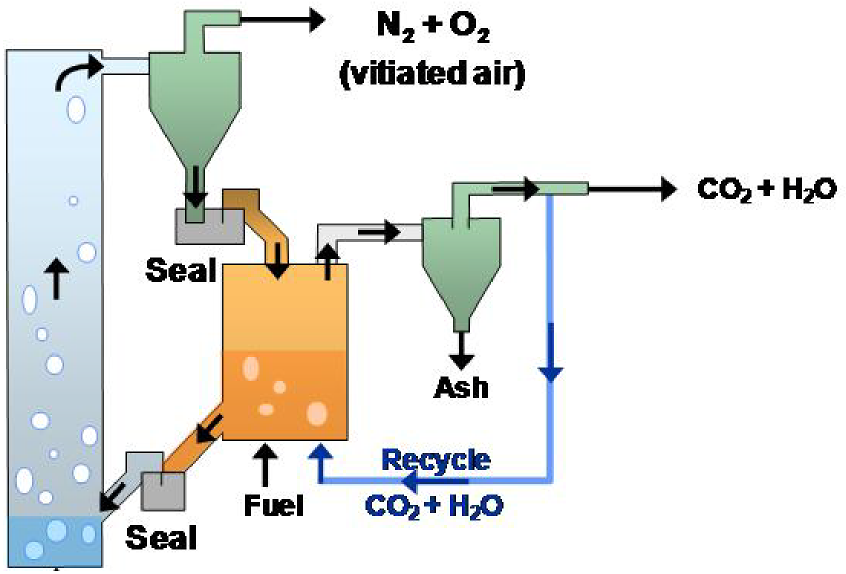
Carrier reaction rate w/oxygen
Carrier reaction rate w/fuel
Carrier degradation

Iterate with more information



ICMI work elements provide the data and analysis.

Element 510 considered relevant industrial applications (next slides)

Defining the Application and Baseline for Economic Studies

Industry - Capture Technology Matrix

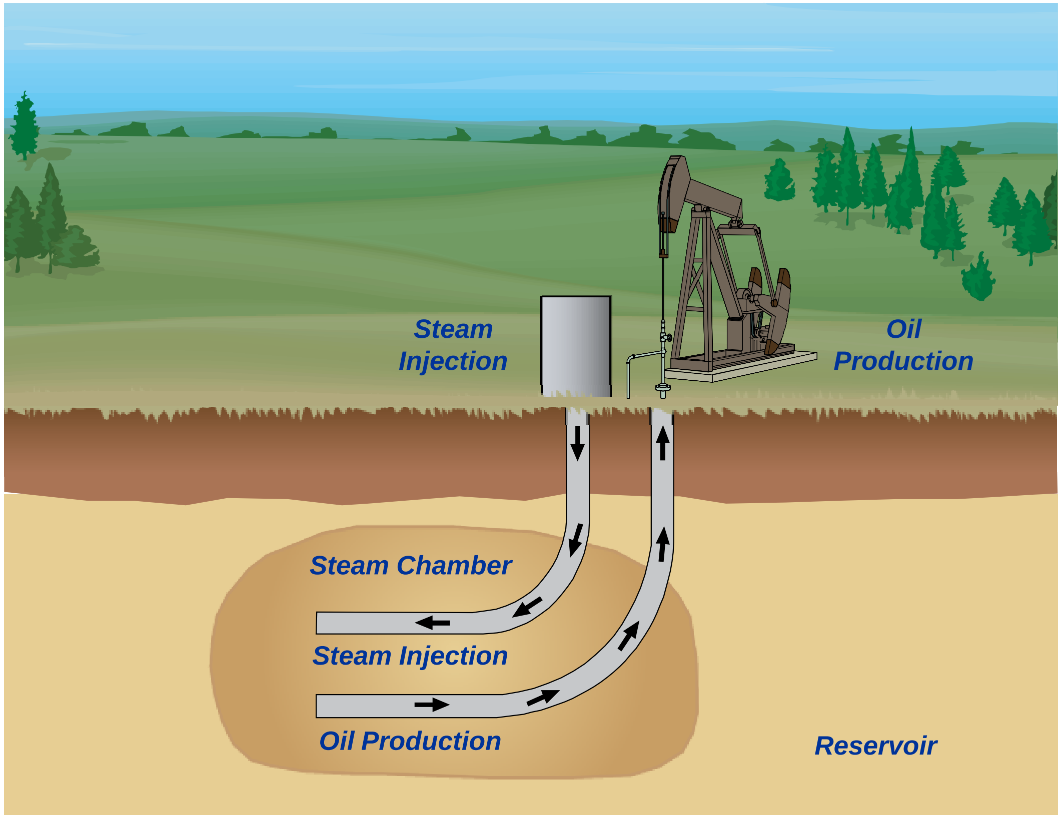
Legend:
- Potential
- Proven
- Preferred
- In Testing
- Capture not Required

	Gas Separation/Post Combustion						Oxyfuel		Pre-Combustion				
	Chemical Solvent	Physical Solvent	Sorbent	Membrane	Carbonate Looping	Cryogenic	Oxyfuel	Chemical Looping Combustion	Chemical Solvent	Physical Solvent	Sorbent	Membrane	Chemical Looping Reforming
Refineries													
Process Heating - N4	Potential		Potential	Potential	Potential		Potential	Potential					
Steam/Utilities - N4	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Hydrogen Production									Potential	Proven	Potential	Potential	Potential
FCC Regeneration	Potential		Potential	Potential			In Testing						
Cement													
Cement Kiln - N2	Potential				Potential		Preferred N1						
Iron & Steel													
Traditional Blast Furnace - N5	Potential	Preferred N3		Potential	Potential		Preferred N3						
DRI									Potential	Proven	Potential	Potential	Potential
Oil & Gas													
O&G Processing	Proven	Proven		Potential		Proven							
O&G Processing Steam/Utilities	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Oil Sands Steam Production - SAGD	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Oil Sands Processing - Hydrogen									Potential	Proven	Potential	Potential	Potential
Oil Sands Processing - Steam	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Ethanol/Ethylene													
Bioethanol via fermentation - N6	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required	Capture not Required
Ethylene	Potential		Potential	Potential	Potential		Potential						
Steam/Utilities	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Pulp & Paper													
Kraft Mills - N5	Potential		Potential	Potential									
Steam and Heat	Potential		Potential	Potential	Potential		Potential	Potential	Potential	Potential	Potential	Potential	Potential
Ammonia/Fertilizer													
Hydrogen Production									Potential	Proven	Potential	Potential	Potential

N1 Will not be suited to retrofit -- new plant only
N2 Pre-combustion not suitable due to lower radiant properties
N3 Oxyfuel with CO_2 removal via solvent
N4 Post Combustion limited due to many point sources
N5 Makes up majority of plants, ~70%
N6 CO_2 from fermentors only (no fuel) -- Produces relatively pure CO_2

Potential Chemical Looping Application

- **Steam Production**
  - In any industrial or commercial facility where boilers are in use
  - Oil Sands production & processing, especially Steam Assisted Gravity Drainage (SAGD) very attractive
  - Oil & Gas production, especially where CO_2 could be used for EOR
- **Electric Power Generation**
  - Need to fully characterize size & complexity of the systems
  - Analysis coordinated with NETL studies of power systems



SAGD Process

Industrial Boiler Steam Conditions

- **Oil Sands SAGD**
  - Saturated steam at 1000 to 1600 psi (Sat temp: 550F to 610F = 290 to 320 C)
  - 500,000+ lb/hr steam rate
  - Fueled by natural gas (could consider pet coke)
- **Oil & Gas Plant**
  - Saturated steam at varying pressure levels (LP [~50 psi] & MP [~300 psi] typical)
  - Variable steam rate
  - Fueled by natural gas
- **Refinery**
  - Saturated steam up to 900 psi pressure levels
  - 500,000+ lb/hr steam rate
  - Fueled by refinery gas
- **Recommendation for future systems analysis work**
  - Evaluate steam generation at 300, 600, 900 and 1500 psi levels
  - Natural gas fuel
  - Compare to SAGD and other industrial / commercial steam systems

Very different than power applications

Establishing a baseline case for an industrial boiler application with capture

Site Description and Conditions

- **Unspecified location**
- **Generic conditions based on ISO specifications**
- **Site specific conditions can impact analysis, but comparisons are valid as long as design conditions are consistent across cases**

Elevation, (ft)	0
Barometric Pressure, MPa (psia)	0.10 (14.696)
Design Ambient Temperature, Dry Bulb, °C (°F)	15 (59)
Design Ambient Temperature, Wet Bulb,°C, (°F)	11 (51.5)
Design Ambient Relative Humidity, %	60

Fuel – Natural Gas

Natural Gas Composition:

Component		Volume Percentage
Methane	CH_4	93.1
Ethane	C_2H_6	3.2
Propane	C_3H_8	0.7
n-Butane	C_4H_{10}	0.4
Carbon Dioxide	CO_2	1.0
Nitrogen	N_2	1.6
	Total	100.0

	LHV	HHV
kJ/kg	47,454	52,581
MJ/scm	34.71	38.46
Btu/lb	20,410	22,600
Btu/scf	932	1,032

Natural Gas Cost:

Baseline Studies: $6.55/MMBtu, June 2007 dollars

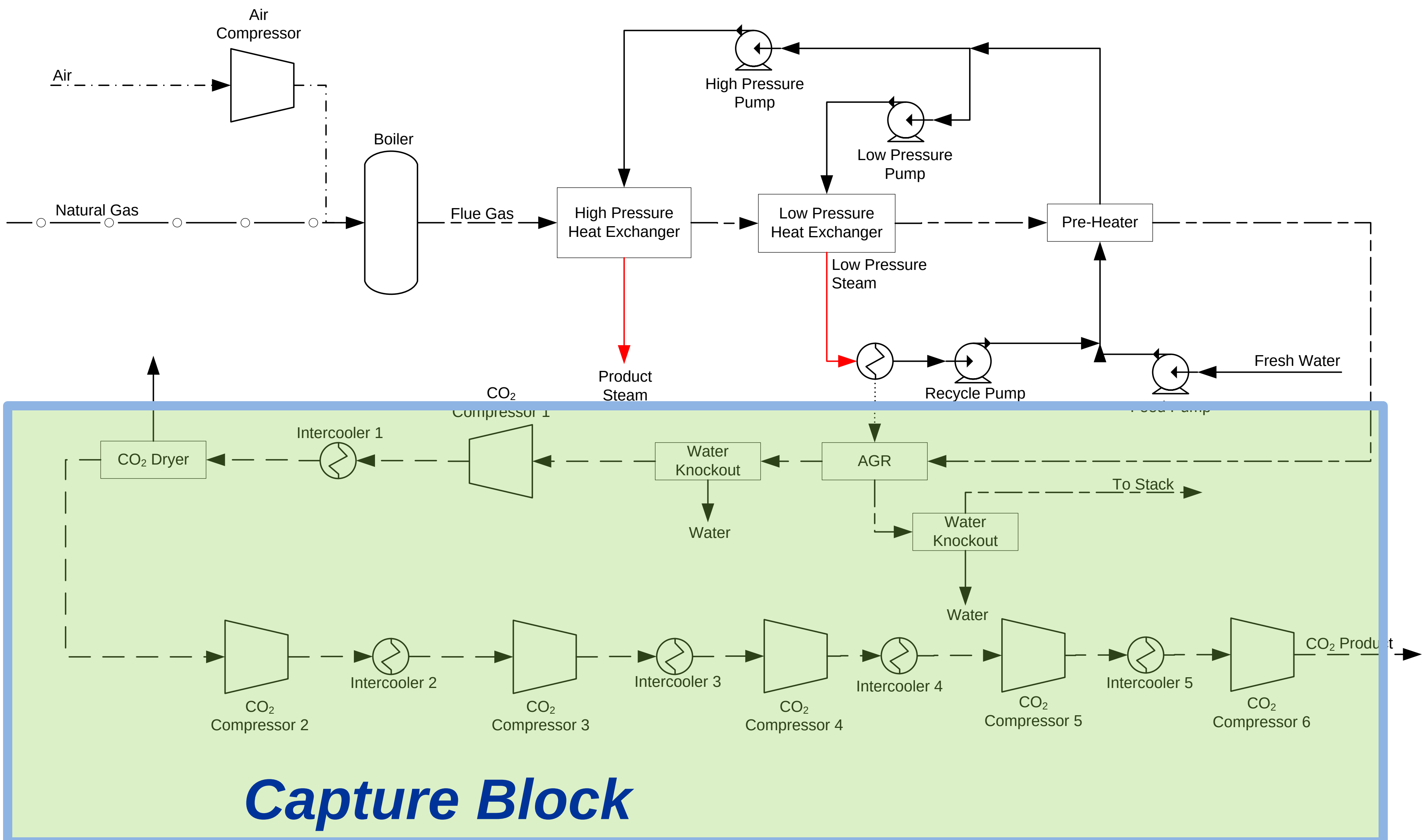
Updated Cost: $6.13/MMBtu, June 2011 dollars

Assumes gas is delivered at 435 psig

Industrial Baseline Application Design

- **Steam Generator Capacity**
  - Case 1: 27,500 lb/hr (~10 MW Thermal)
  - Case 2: 275,000 lb/hr (~100 MW Thermal)
  - Steam is generated at 600 psi with 100°F of superheat
  - 80% boiler efficiency
- **Steam Generator Sparing Philosophy**
  - Assume no sparing
- **Reference Steam Generation Process**
  - Watertube Design (Characterization of the U.S. Industrial Commercial Boiler Population - large watertube boilers account for most steam production)
- **Carbon Capture**
  - Amine Scrubber

Industrial Reference Case Block Diagram



Industrial Reference Case Performance

- **Heat rate was assumed to be natural gas feed and steam production was held constant on capture cases**

	10 MW_{TH}	**12.4 MW_{TH}**	**100 MW_{TH}**	**124.4 MW_{TH}**	
	No Capture	**Capture**	**No Capture**	**Capture**	**Units**
Auxiliary Load					
Boiler Feedwater Pumps	20	20	180	190	kWe
Amine System Auxiliaries	0	100	0	1,100	kWe
Circulating Water Pump	0	40	0	330	kWe
Ground Water Pumps	4	10	40	70	kWe
CO_2 Compression	0	170	0	1,710	kWe
Cooling Tower Fans	0	20	0	170	kWe
Air Compressor	40	40	350	440	kWe
Total	**64**	**400**	**570**	**4,010**	**kWe**
Plant Performance					
Net Auxiliary Load	64	400	570	4,010	kW_e
Net Plant Efficiency (HHV)	0.838	0.647	0.838	0.647	Fraction
Net Plant Efficiency (LHV)	0.928	0.717	0.928	0.717	Fraction
Natural Gas Feed Flow	685 (1,510)	852 (1,879)	6,848 (15,098)	8,522 (18,788)	kg/hr (lb/hr)
Thermal Input (HHV)	9,977	12,416	99,774	124,160	kW_{th}
Thermal Input (LHV)	8,996	11,195	89,959	111,946	kW_{th}
600 psia Steam Produced	23,175	23,175	231,754	231,754	lb/hr
73.5 psia Steam Required	0	7,798	0	77,978	lb/hr
Raw Water Consumption	23,175	23,175	231,754	231,754	lb/hr

Notice the efficiency

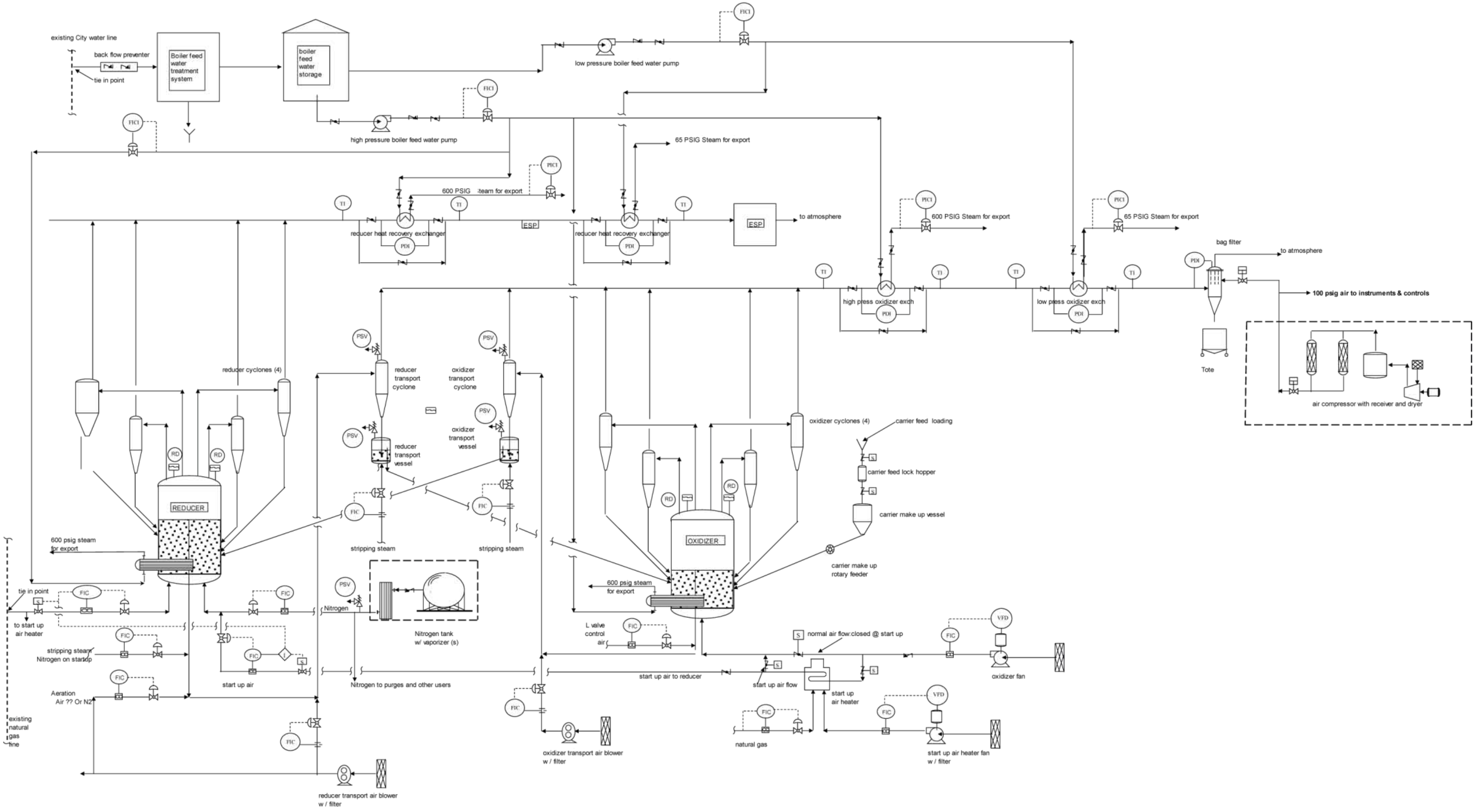
Chemical Looping Application Analysis
10 MW_{th} and 100 MW_{th}

Key Model Assumptions Initially Applied

- **Reducer reactor type:**
  - Bubbling fluid bed/turbulent fluid bed
- **Oxidizer reactor type:**
  - Bubbling fluid bed/circulating bed
- **Fluid bed gas-carrier contact: plug flow (optimistic)**
- **Carrier type: Fe_2O_3 on alumina support**
- **Carrier particle size: 0.15 mm**
- **Carrier reaction resistances: only shrinking grain resistance**
- **Solids transport: dilute pneumatic transport for bubbling bed case/none for circulating bed case**

P&ID Sketch 100 MW CLC

NETL IMCI 100 MW CLR
P&I scoping sketch
W.O. 30369-296.6.600.007.002.520
BY R. A. Malinak
Checked by B Kovatch
print date = 7/9/2012



Approximate Sizes

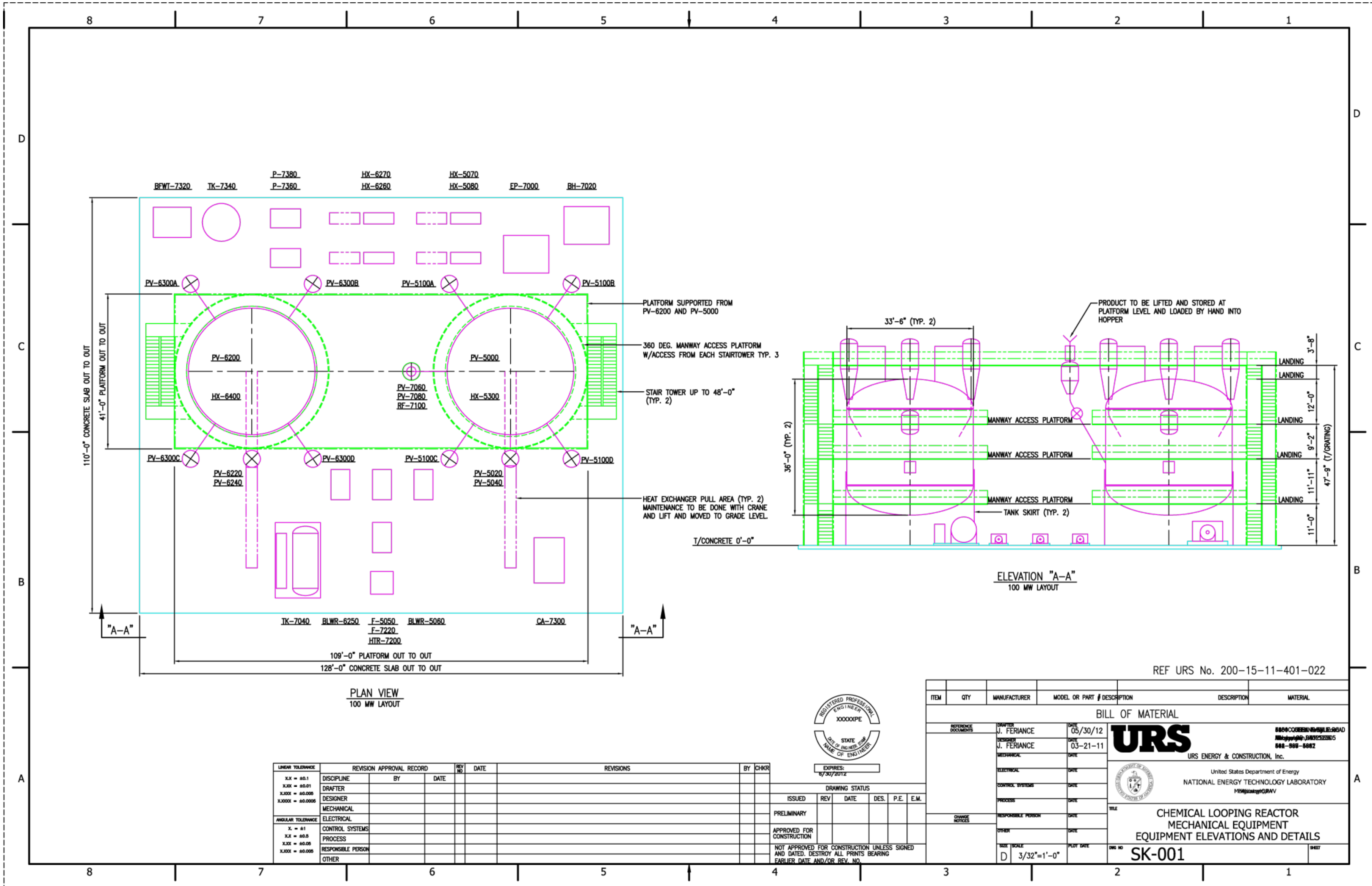
Based on existing data; subject to revisions with other carriers/reactor concepts

	Reducer: Bubbling Beds		Oxidizer: Bubbling Beds	
Natural Gas Input (MW_{th})	10	100	10	100
Vessel diameter (ft)	4.3	10.7	11.5	33.5
Vessel height (ft)	43	38	43	38
Bed height (ft)	23	11	7	7
Bed outlet velocity (ft/s)	17	17	4	4
Cyclone number	1	4	2	4
Cyclone diameter (ft)	3.6	5.1	11.2	25.0
Cyclone height (ft)	13	20	16	36
Solids transport cyclone diameter (ft)	3.1	7.7	3.1	7.7
Solids transport cyclone height (ft)	11	34	16	36
Baghouse length and width (ft)	7	17	10	28
Baghouse height (ft)	20	20	20	20
HRSG diameter (ft)	2.0	6.3	2.7	8.5
HRSG length (ft)	20	20	30	30

Process Performance

CLC Design Concept	BUBBLING FLUID BEDS, PLUG FLOW GAS		CIRCULATING OXIDIZER, TURBULENT REDUCER PLUG FLOW GAS	
Natural Gas Feed Rate (MWth, HHV)	10	100	10	100
PROCESS HEAT BALANCE				
Natural gas energy input (MMBtu/hr, HHV)	**34.12**	**341.20**	**34.12**	**341.20**
Total product steam generation (MMBtu/hr)	**26.72**	**270.19**	**27.37**	**284.98**
Reducer vessel product steam generation (MMBtu/hr)	0.00	0.00	0.00	0.00
Oxidizer vessel product steam gen (MMBtu/hr)	15.26	152.60	16.78	167.80
Reducer CO2 offgas product steam generation (MMBtu/hr)	3.85	38.65	3.89	38.95
Oxidizer offgas product steam generation (MMBtu/hr)	7.61	78.94	6.71	78.22
Oxidizer offgas stripping steam generation (MMBtu/hr)	**0.29**	**2.90**	**0.29**	**2.90**
Vessel heat losses (MMBtu/hr)	**0.94**	**4.39**	**1.87**	**4.94**
CO2 product stream unburned fuel (MMBtu/hr, HHV)	**0.47**	**4.66**	**0.47**	**4.65**
Flue gas, CO2 product and vent streams sensible heat	**5.70**	**59.07**	**4.12**	**43.73**
Boiler Efficiency based on product steam (%, HHV)	**78.3**	**79.2**	**80.2**	**83.5**

Layout 100 MW CLC (110’ x 128’ x 50’)



Where and <u>how</u> can chemical looping work?

Industrial applications (includes NG, smaller scale)

Power applications (coal, 100+MW scale)

Iterate with more information

Attributes:
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System issues & configuration
Heat and material balances
Attrition
Material supply & handling
Heat exchanger/integration
Sensors and control
Emissions
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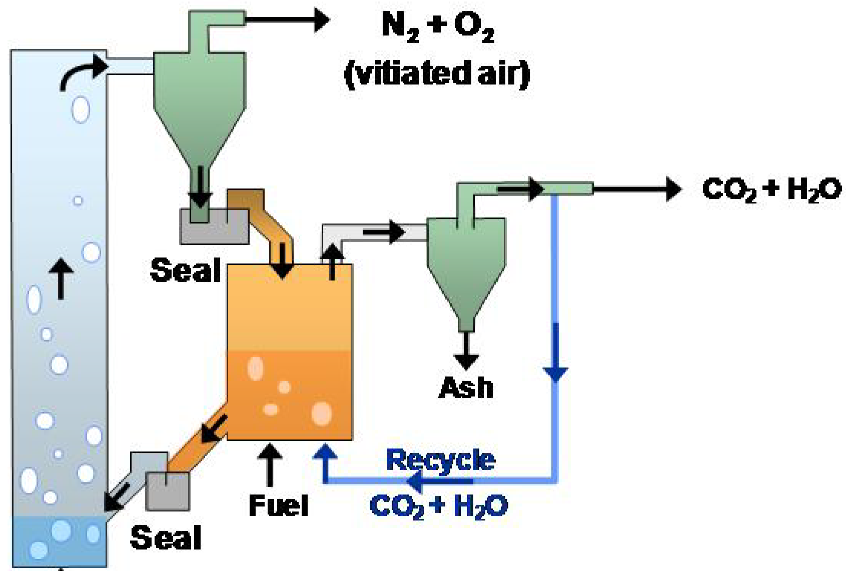
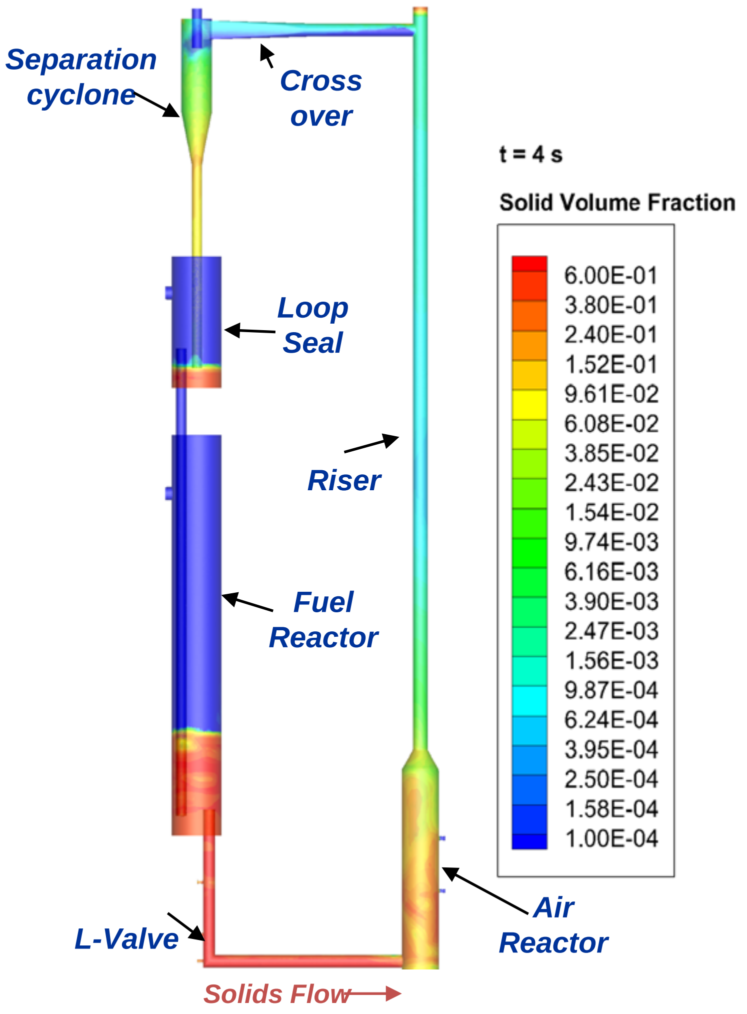


ICMI work elements provide the data and analysis.

These data will enable CCSI scale-up simulation.

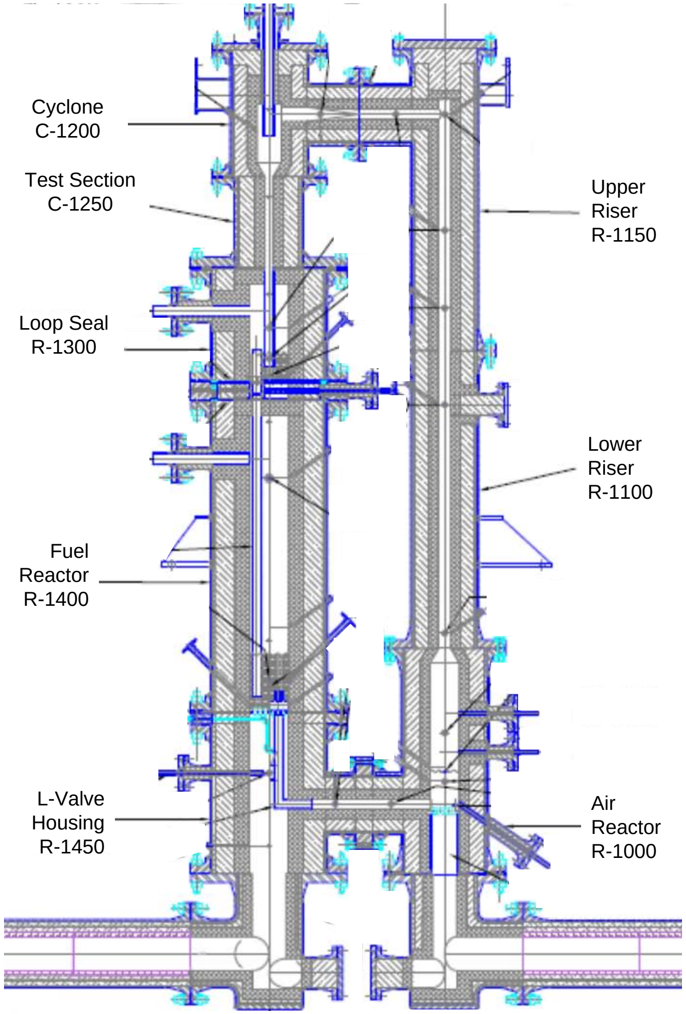
Detailed Modeling Tools

- **Low-Fidelity Model**
  - Excel based model used to validate basic material and energy balance of CLR
  - Includes pressure drop calculations and computed Heat & Material balance for at least five operating conditions Important to affirm that the solids circulate as desired.
- **High-Fidelity CFD**
  - “Cold Flow” simulations complete, awaiting experimental validation
  - “Hot Flow” simulations have been constructed
  - Gen 1 kinetics and 3 baseline operating conditions underway



CLR whole system – 3D, front view

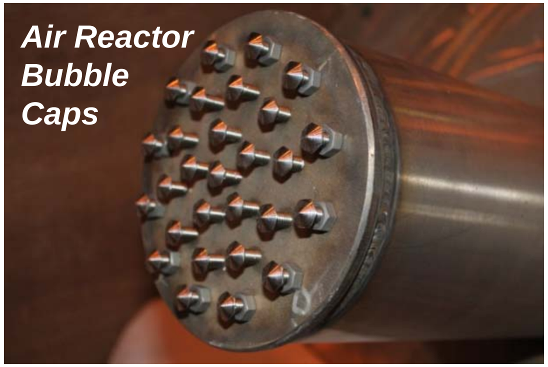
Validating the Predictions:
Laboratory Scale Chemical Looping Reactor (CLR)



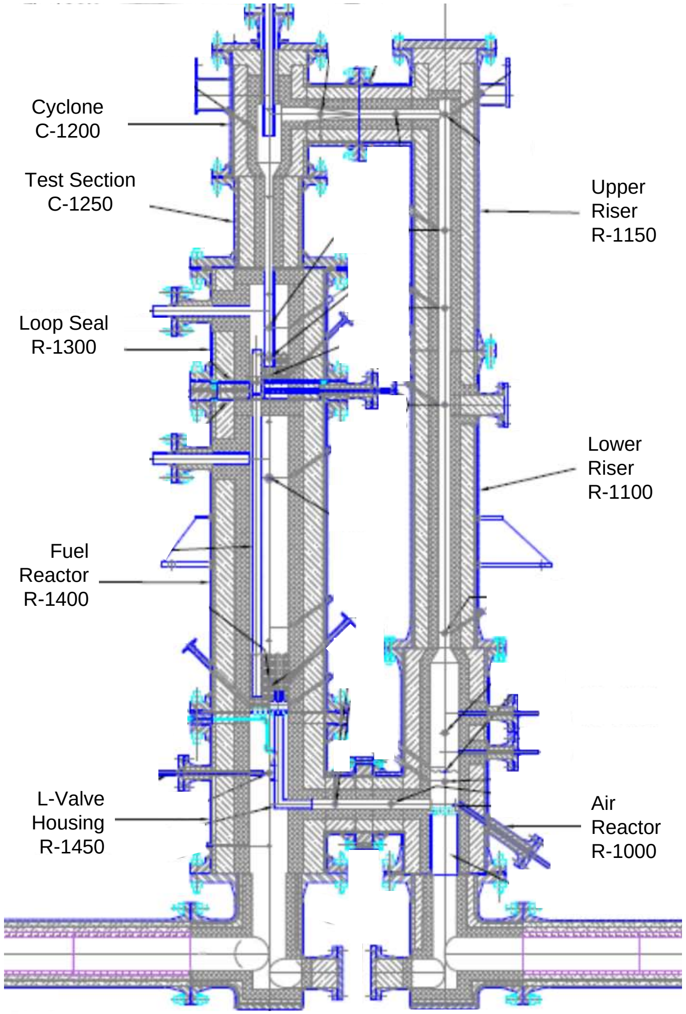
Current Status: Being Installed at NETL

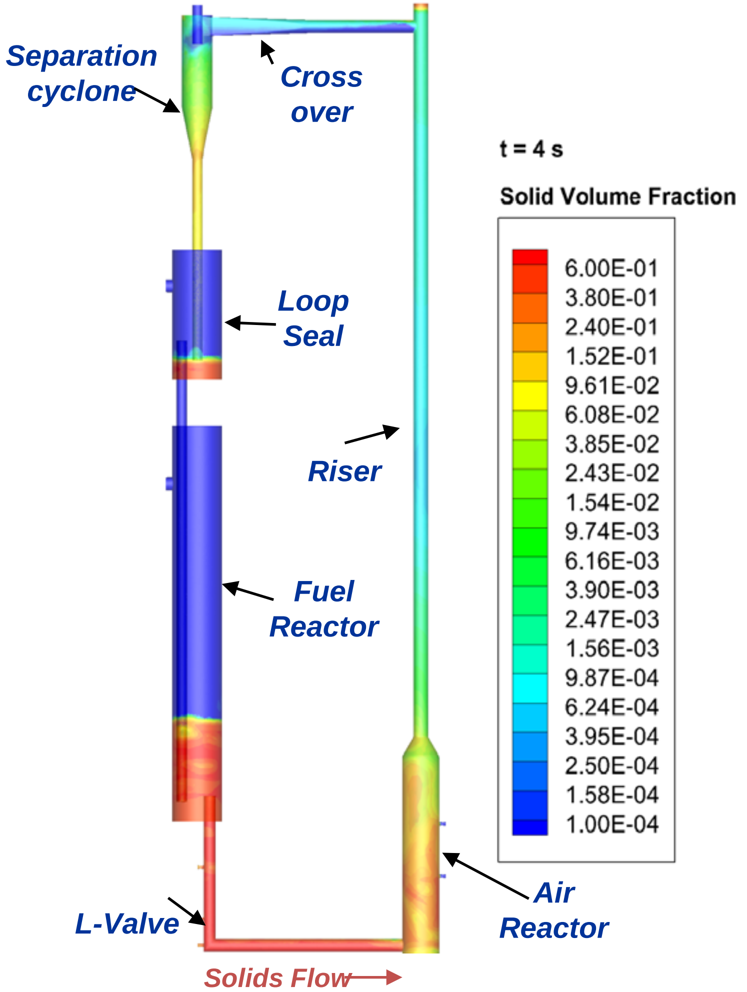
CLR Vessels Delivered to NETL

Project Structure



Validating the Predictions: Laboratory Scale Chemical Looping Reactor (CLR)





Non-Reacting Cold Flow Unit

- Used to simulate and characterize the behavior of solids transfer and the control of oxygen carrier particles.
- Measured characteristics: gas-particle velocity fields, 3-D solid-void fraction distributions, bubble size, bubble frequency.
- Geometry and flow match the hot unit except for the temperature.
- Acrylic construction allows for visual identification of the flow structures and use of advanced instruments such as high speed particle imaging velocimetry.
- Provides hydrodynamic validation data for various models and provides a similar system to explore control strategies.

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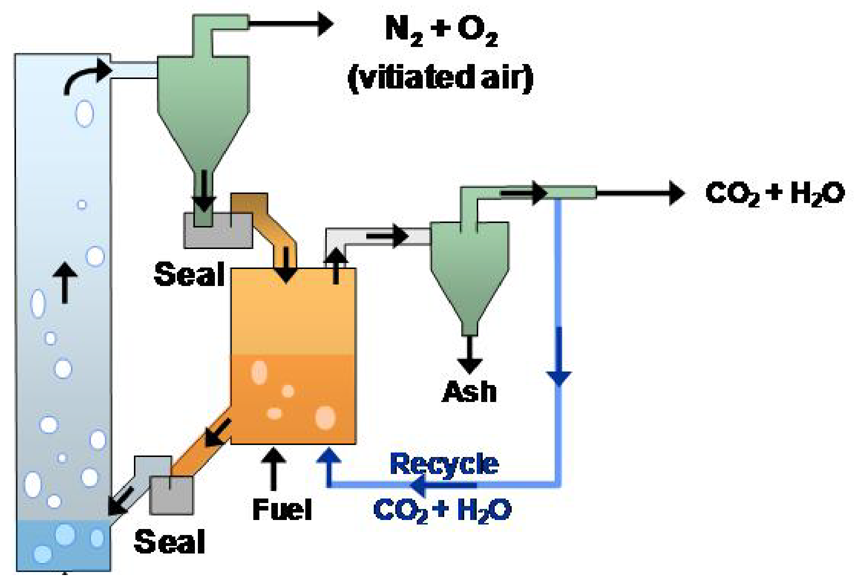

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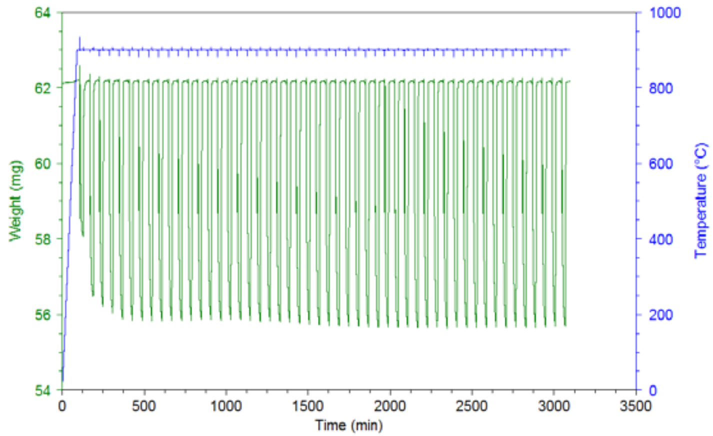
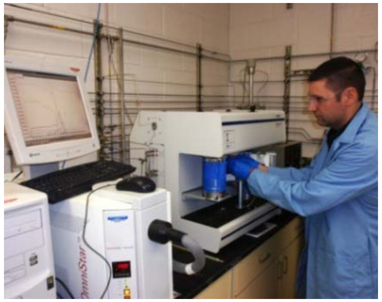
Oxygen Carrier Development

- ***Carriers for CLR study have been identified and full report on screening study is available***
  - *Hematite – natural ore*
  - *Cu-Fe/Al2O3 - synthetic material*
    - *Mixed-metal oxides developed at NETL*
- ***Vendors have been identified to provide materials***
- ***Quality testing underway on vendor-supplied hematite***



Example of TGA cycle studies shows good stability and oxygen capacity

	Reduction rate (min^{-1})	Oxidation rate (min^{-1})	Oxygen transfer capacity (%)
Ilmenite	0.18	0.49	4.6
Hematite	0.33	0.52	10



Attrition Unit Shakedown Using Alumina Powder

Attritted particles should show up here.

Boring is Better !

Summary

- ***Industrial Carbon Management Initiative :*** **technologies and validated simulation tools for carbon capture and storage from industrial sources:**
  - **Chemical Looping (CL) as a capture technology**
  - Depleted shale gas reservoirs for CO_2 sequestration
  - Basic research in conversion of CO_2 to useful chemicals using light or waste heat
- **Research in progress covers**
  - Economic analysis of promising industrial CL applications
  - Development of oxygen carriers and reactor configurations
  - Validation of numeric models for detailed simulations & scale-up
- **Commercial and research interest is welcome!**

ICMI Reports (contact NETL)

- 2011 Annual Report on ICMI Project
- Literature Survey of Kinetic Parameters Relevant to Chemical Looping Combustion
- Chemical Looping Kinetic Rate Model
- Literature Review of Attrition Testing
- Literature Review of Solid-Solid Separation
- Evaluation of Commercially Available Solids Flow Sensors and Technologies for Chemical Looping Application
- Oxygen Carrier Development for Chemical Looping Combustion with Natural Gas Literature Review
- The Development of Applicable Oxygen Carrier Materials for Chemical Looping Combustion Using Methane as Fuel
- Modeling Lifetime of Corrodible Components Literature Review
- Hydrogen Production Screening Study
- Ca-Sorbent Development for Carbon-neutral Industrial Gas Production of Hydrogen Using Ca Looping
- Design Basis for Storage of CO_2 in Depleted Shale Gas Reservoirs
- CFBC Furnace Temperature and Other Considerations