Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems

primary project goals

Southern Research Institute (SR) is developing a combined magnesium oxide (MgO)-based carbon dioxide (CO_2) sorbent/water-gas shift (WGS) reactor that offers high levels of durability, simplicity, flexibility, and heat management ability. The primary project goal is to develop a combined CO_2 sorbent/WGS reactor-based process with advanced integrated heat management to capture 90% of the CO_2 from the Transport Reactor Integrated Gasifier (TRIG™) syngas for integrated gasification combined cycle (IGCC) applications.

technical goals

- Identify sorbent and operation conditions for a combined CO_2 sorbent/WGS reactor through modeling and experimental study of the WGS reaction at bench scale.
- WGS reaction conversion extent of 90 to 95% of equilibrium carbon monoxide (CO) conversion.
- Carbon dioxide capture from coal gasification syngas at a temperature of 350°C and pressure of 40 atmosphere (atm), with syngas throughput at space velocity of 500 to 2,000 standard cubic centimeter (scc)/g/hr (for sorbent), 1,000 to 4,000 scc/cc/hr (for catalyst).
- Carbon dioxide capacity of sorbent 3 to 5 mol/kg, and regenerability and durability of more than 500 cycles.
- Progress toward enabling combined MgO-based CO_2 sorbent/WGS reactor technology in a 550-megawatt-electric (MWe) IGCC plant, capable of 90% capture of CO_2 at over 95% purity, while reducing the cost of electricity (COE) by 30% over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily hydrogen [H_2] and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced in whole by a combined MgO-based CO_2 sorbent/WGS reactor unit. Within the WGS reactor, CO_2 would be withdrawn directly by the sorbent, efficiently increasing the driving force for the equilibrium WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor (or banks of reactors in parallel as syngas throughput requires).

technology maturity:

Laboratory-Scale, Simulated Syngas

project focus:

Combined CO_2 Sorbent/Water-Gas Shift Reactor

participant:

Southern Research Institute

project number:

FE0026388

predecessor projects:

N/A

NETL project manager:

Andy Aurelio
isaac.aurelio@netl.doe.gov

principal investigator/ responsible person:

Santosh Gangwal/
Amit Goyal
Southern Research Institute
agoyal@southernresearch.org

partners:

IntraMicron Inc., Nexant Inc.

start date:

10.01.2015

percent complete:

100%

The CO_2 sorbent is stabilized meso-porous high-surface area MgO promoted by alkali salts. Magnesium oxide captures CO_2 according to reactions 1 through 3. Carbon dioxide is present in the syngas from the original gasification reactions, and is additionally formed as a product of the WGS reaction (reaction 4):

$$MgO(s) + CO_2(g) \leftrightarrow MgCO_3(s);\ \Delta H = -100.7\ KJ/mol \tag{1}$$

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s);\ \Delta H = -81.1\ KJ/mol \tag{2}$$

$$Mg(OH)_2(s) + CO_2(g) \leftrightarrow MgCO_3(s) + H_2O(g);\ \Delta H = -19.5\ KJ/mol \tag{3}$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g);\ \Delta H = -41.2\ KJ/mol \tag{4}$$

The MgO sorbent gradually transforms to carbonate in the forward reactions and must be regenerated to MgO in the reverse reactions to enable ongoing operation. Accordingly, the reactor must be operated in cyclic mode, with combined WGS reaction/CO_2 capture interval followed by a regeneration interval, with multiple reactors needed to maintain continual process operation. The regeneration is accomplished by reverse gas flow through the reactor at decreased pressure (atmospheric). Therefore, this can be regarded as a pressure swing adsorption system for CO_2 capture.

This technology takes advantage of IntraMicron's technology of Microfibrous Entrapped Catalysts (MFECs). These are based on microfibrous media (MFM), a highly porous structure (≈94%) that consists of randomly oriented microfibers. The random orientation of the microfibers provides a uniform flow profile throughout the bed, which minimizes channeling, assists with mixing, and generally allows improved fluid flow to facilitate mass transport at catalytic reaction sites. MFECs are prepared using a proprietary method that locks small catalyst particles (0 to 35 vol. %, and with size 40 to 300 microns) within the microfibrous media, as depicted in Figure 1(a). The microfibrous structure can be formed from a variety of materials, including metals (copper [Cu], nickel [Ni], etc.), alloys (stainless steel, brass), polymers, and glass, allowing the support structure to be tailored to a given reaction system. Metals are typically used when enhanced heat transfer is needed, because high-conductivity metal MFM enable rapid heat transfer to or from the embedded catalyst particles. As such, this technology is helpful in intensifying catalytic processes where catalyst performance is otherwise limited by heat transfer limitations. Also, distributing catalyst particles on a highly porous structure allows gas flow more akin to a fluidized bed than a packed bed; this might be termed "frozen-fluidized bed" to distinguish it from the conventional alternatives.

Conventional WGS reactors have the catalyst in traditional packed beds, and it is believed that significant advantages can be realized by performing the WGS reaction using MFECs in the frozen-fluidized bed configuration (Figure 1(c), which would reduce or eliminate intra-particle heat and mass transfer limitations experienced conventionally. For example, Figure 1(b) shows the better heat transfer in MFM as compared to a conventional packed bed of alumina.

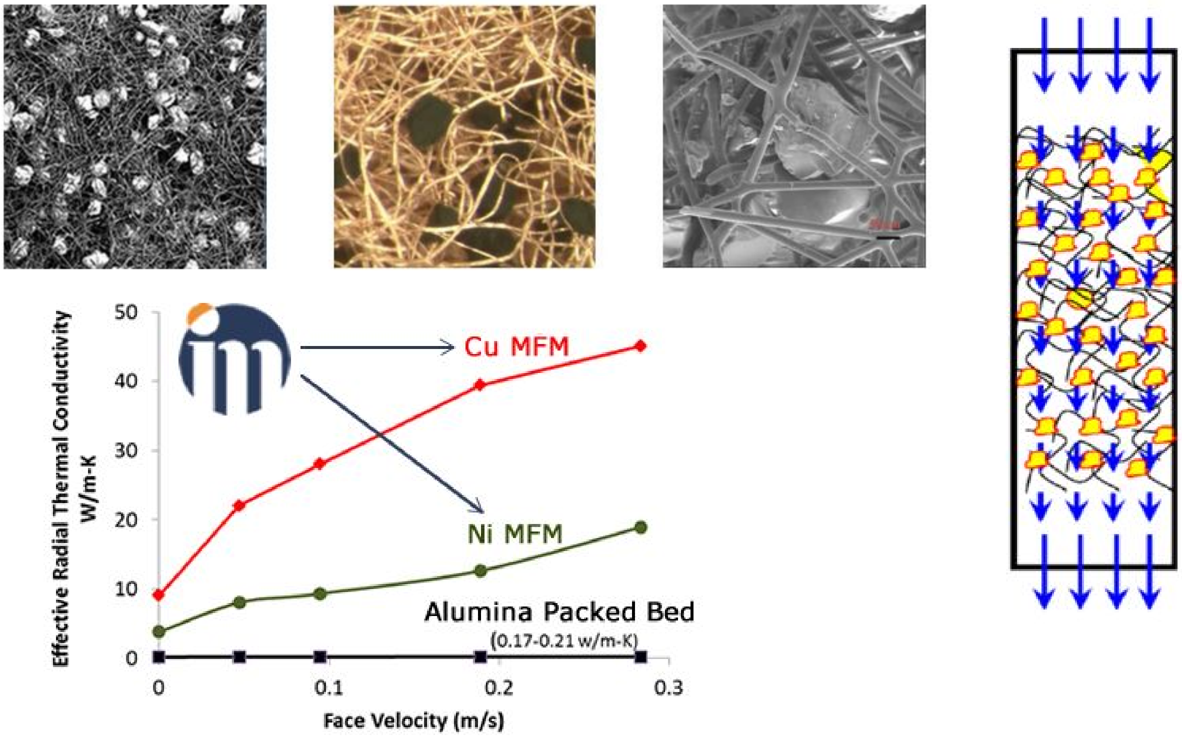


Figure 1: (a) Images of catalyst and sorbent particles entrapped in sintered microfibrous media (top left); (b) comparison of thermal conductivities of metal MFEC with alumina packed bed (bottom left); (c) improved gas flow through frozen fluidized bed configuration of MFECs (on right).

In the SR application, commercial WGS catalyst is used as the source material for the catalyst particles in the MFECs. Promoted MgO sorbent particles are also introduced into the MFM. The result consists of finely divided sorbent and catalyst particles in close proximity, which allows good heat transfer characteristics and gas flow through the mesh holding them.

Although combining the WGS reaction and CO_2 capture in the same media provides intrinsic process intensification, it does create challenges in terms of the inevitable regeneration cycle demanded by the sorbent. The WGS catalyst is present in the reactor as the sorbent undergoes regeneration; the WGS catalyst obviously experiences no benefit from the regeneration cycle and could experience degradation due to some conditions applied for regeneration.

Figure 2 depicts the laboratory-scale apparatus that SR has employed to determine performance characteristics of the combined WGS/MgO sorbent media in a small MFEC reactor, operated on simulated syngas compositions resulting from an air-blown TRIG™ gasifier and an oxygen-blown GE gasifier.

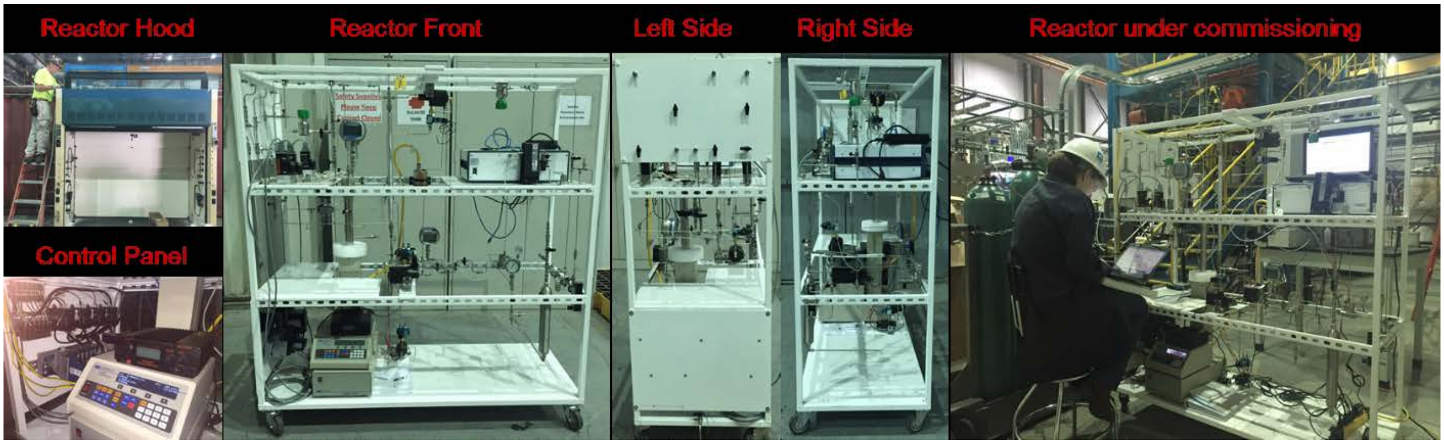


Figure 2: SR's bench-scale CO_2 reactor system.

In experimental evaluation of the bench-scale MFEC reactor, SR discovered desulfidation of WGS catalyst resulting in reduced CO conversion activity and observed structural changes in copper metal MFEC. The sulfidation caused reduction of thermal conductivity and creation of hot spots. Desulfidation with steam caused degradation of fibrous structure. These problems were addressed by modifications of the reactor system to prevent regeneration steam from affecting the catalyst bed by changing MFEC materials from copper to stainless steel and further optimizing reaction conditions.

Under optimized conditions, the sorbents achieved up to 8 mmol/g of CO_2 working capacity and remained stable over 500 cycles of adsorption and regeneration. The selected WGS process achieved 96% CO per pass conversion and remained isothermal during the test duration that lasted more than 500 cycles.

Figure 3 shows the concept for integration of this technology in the context of a representative IGCC process cycle, indicating the primary process flows and their temperatures for both absorption and regeneration of the WGS-MgO reactors. Based on this general process arrangement for inclusion of the SR technology in an IGCC cycle with carbon capture, techno-economic analyses (TEAs) have been prepared comparing this to U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) baselines of a GE gasifier-based IGCC cycle with capture and a subcritical pulverized coal plant with capture. Results are reported in Figure 4. Overall, given known performance parameters and assumptions for costs, the SR MFEC-based WGS/CO_2 capture process has lower overall investment costs than the comparative IGCC baseline, but suffers from lower gross power output and therefore yields approximately the same COE as the baseline IGCC case.

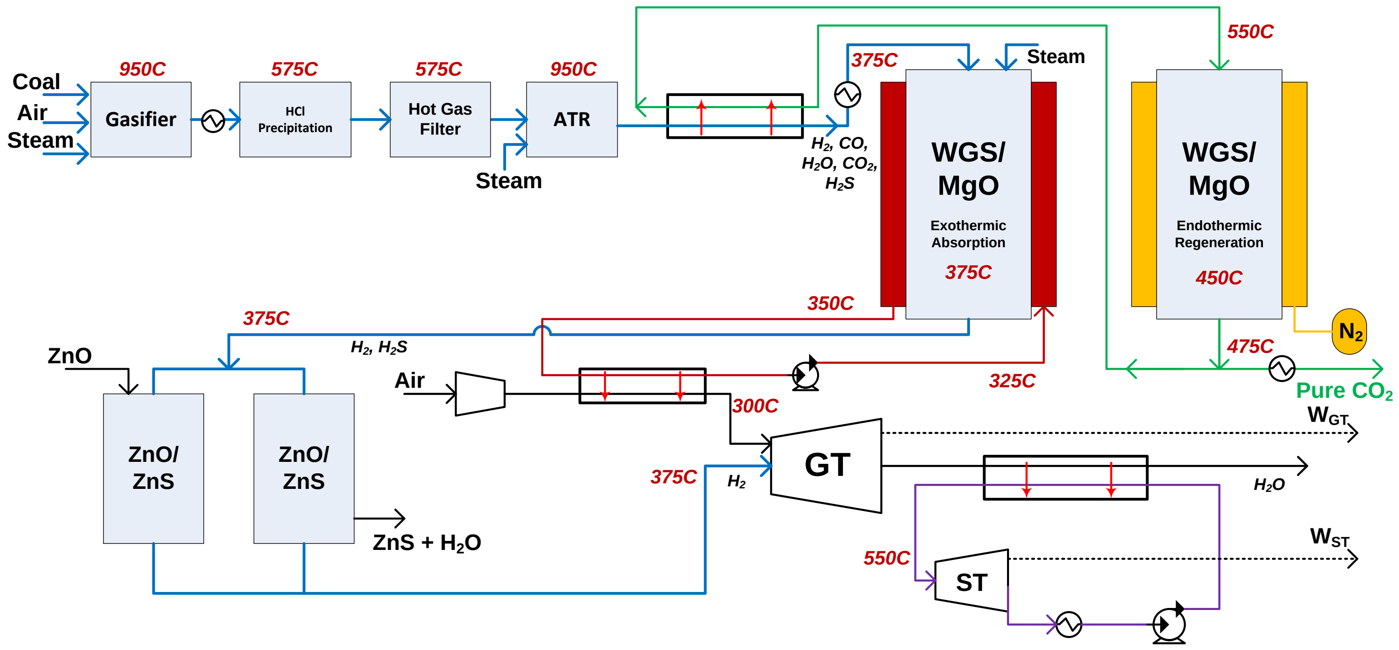


Figure 3: Integration of the combined sorbent/WGS-based CO_2 capture process in context of an IGCC plant cycle.

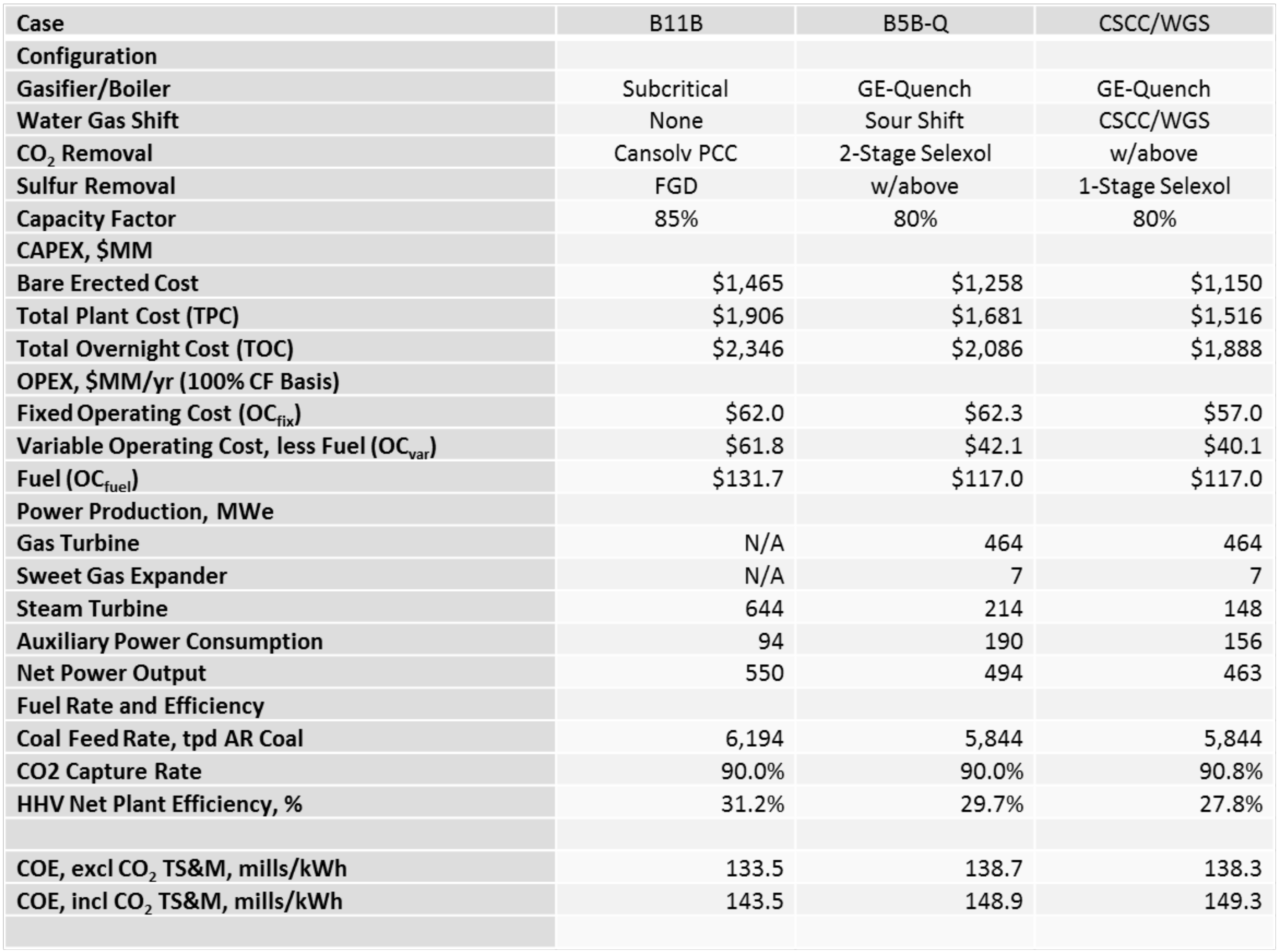
At the end of technology and process development efforts, SR concludes that the combined WGS/CO_2 capture process has technical feasibility to replace conventional two- to three-stage WGS reactor systems with intercooling plus a separate CO_2 capture unit with a single WGS reactor unit, with potential for energy efficiency increase and equipment cost savings.

Notwithstanding the above finding, SR concluded that a single WGS reactor coupled to multiple CO_2 sorbent beds would be a preferred commercial approach compared to several mixed-adsorption/WGS reactors, after considering the comparative implications of these process arrangements. It turns out that high-CO conversions approaching 96% can be achieved in the WGS reactor containing only the WGS catalyst supported on MECS and thereby made to be isothermal. In this case, sorbent-only reactors would be located downstream for CO_2 capture. This configuration would meet capture performance requirements but be less complicated in terms of sorbent regeneration (obviously, because regenerating a dedicated sorbent-only reactor with steam is not problematic, which regenerating one containing combined WGS catalyst and sorbent would deleteriously expose the WGS catalyst to steam).

In all cases, heat management using MFECs was demonstrated to enable thermodynamically favorable reaction temperatures for both exothermic CO_2 capture/WGS and endothermic regeneration.

The current state-of-the-art CO_2 capture process involves scrubbing the gas stream at low temperature. SR's elevated-temperature CO_2 capture technique eliminates the need to cool the gas stream coming from WGS reactor, resulting in thermodynamic advantage.

SR's high-capacity CO_2 sorbent provides fast adsorption/desorption kinetics, but regeneration with steam causes slow degradation that needs further investigation.



Case	B11B	B5B-Q	CSCC/WGS
Configuration			
Gasifier/Boiler	Subcritical	GE-Quench	GE-Quench
Water Gas Shift	None	Sour Shift	CSCC/WGS
CO_2 Removal	Cansolv PCC	2-Stage Selexol	w/above
Sulfur Removal	FGD	w/above	1-Stage Selexol
Capacity Factor	85%	80%	80%
CAPEX, $MM			
Bare Erected Cost	$1,465	$1,258	$1,150
Total Plant Cost (TPC)	$1,906	$1,681	$1,516
Total Overnight Cost (TOC)	$2,346	$2,086	$1,888
OPEX, $MM/yr (100% CF Basis)			
Fixed Operating Cost (OC_{fix})	$62.0	$62.3	$57.0
Variable Operating Cost, less Fuel (OC_{var})	$61.8	$42.1	$40.1
Fuel (OC_{fuel})	$131.7	$117.0	$117.0
Power Production, MWe			
Gas Turbine	N/A	464	464
Sweet Gas Expander	N/A	7	7
Steam Turbine	644	214	148
Auxiliary Power Consumption	94	190	156
Net Power Output	550	494	463
Fuel Rate and Efficiency			
Coal Feed Rate, tpd AR Coal	6,194	5,844	5,844
CO2 Capture Rate	90.0%	90.0%	90.8%
HHV Net Plant Efficiency, %	31.2%	29.7%	27.8%
COE, excl CO_2 TS&M, mills/kWh	133.5	138.7	138.3
COE, incl CO_2 TS&M, mills/kWh	143.5	148.9	149.3

Figure 4: TEA case comparisons.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
Pellet Density	kg/m^3	1,700	1,600
Bulk Density	kg/m^3	1,100	1,050
Average Particle Diameter	µm	150	150
Packing Density	kg/m^3	750	730
Sorbent Heat Capacity	kJ/kg-K	0.93	0.93
Manufacturing Cost for Sorbent	$/kg	0.47	TBD
Adsorption			
Total pressure	bar	40	40
Temperature	°C	350	350
Equilibrium Loading	g mol CO_2/kg	7.2	5.6
Heat of Adsorption	kJ/mol CO_2	-130	-130
Desorption			
Total pressure	bar	1	1
Temperature	°C	390	350
Heat of Desorption	kJ/mol CO_2	130	130

Definitions:

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Packing Density – Ratio of the active sorbent mass to the total adsorber volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figure 3 above.

Syngas Conditions – Pressure, temperature and composition of the gas entering the reactor, TRIG™ (air-blown) case:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	8.5	17.5	2.6	50.5	11.7	9.2	500

Pressure, temperature, and composition of the gas entering the reactor, GE (oxygen-blown) case:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	13.7	35.8	0.12	0.8	34.2	15.4	500

technology advantages

- Could replace conventional two-stage WGS reactor system with intercooling plus a separate CO_2 capture unit with a single WGS reactor unit, with potential for energy efficiency increase and equipment cost savings.
- Carbon dioxide capture drives equilibrium-limited WGS toward CO_2 and H_2.
- Integrated heat management maintains thermodynamically favorable reaction temperatures for both exothermic CO_2 capture/WGS and endothermic regeneration.
- The current state-of-the-art CO_2 capture process involves scrubbing the gas stream at low temperature. SR's elevated-temperature CO_2 capture technique eliminates the need to cool the gas stream coming from WGS reactor
- SR's high-capacity and highly regenerable CO_2 sorbent provides fast adsorption/desorption kinetics, which can be applied in a pressure swing process under minimum temperature swing condition.

R&D challenges

- High levels of CO and CO_2 in syngas.
- Effect of contaminants in coal syngas on MFECs, MFECs' thermal stability, and product selectivity maintained at high pressures and temperatures.
- Sorbent capacity, kinetics, and durability.
- WGS catalyst degradation during cycling.
- Heat management in reactor.
- Process integration with IGCC.
- Scale-up and integration given the large number of reactor modules needed to service a 550-MWe plant.

status

The project is complete. The hybrid CO_2 capture/WGS reactor has been run for hundreds of cycles at bench scale and testing has shown the sorbent to meet both CO_2 capture capacity and durability targets. WGS performance was close to target. Reactor modeling and techno-economic evaluation have been completed, and a 1,000-cycle test has been completed to gauge durability at optimum process conditions.

available reports/technical papers/presentations

Zhao S, McCabe K. and Gangwal, S. "*Combined Sorbent/WGS-based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," Final Scientific/Technical Report, April 2019.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Santosh Gangwal, Southern Research Institute, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Combined Magnesium Oxide/Water Gas Shift-Based CO_2 Capture Process,*" poster presentation at CO_2 Summit II: Technologies and Opportunities Conference, Santa Ana Pueblo, New Mexico, April 2016.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," project kickoff meeting presentation, October 2015.