DEVELOPMENT AND EVALUATION OF A NOVEL INTEGRATED VACUUM CARBONATE ABSORPTION PROCESS

primary project goals

The Illinois State Geological Survey (ISGS) set out to prove the novel Integrated Vacuum Carbonate Absorption Process (IVCAP) concept and further improve the energy efficiency of the process for post-combustion carbon dioxide (CO_2) capture.

technical goals

- Test the proof-of-concept of the IVCAP.
- Identify an effective catalyst for accelerating CO_2 absorption.
- Identify an effective additive for reducing the stripping heat.
- Evaluate a modified IVCAP as a multi-pollutant control process for combined sulfur dioxide (SO_2) and CO_2 capture.

technical content

The proposed IVCAP employs a potassium carbonate (K_2CO_3) aqueous solution for CO_2 absorption. While the absorption takes place at atmospheric pressure, the stripper is operated under a vacuum condition. As seen in Figure 1 and Table 1, the low heat of reaction between CO_2 and K_2CO_3 favors a stripping process operated at a low temperature and the low-quality steam (close to the exhaust end of low-pressure turbine in the power plant) can be used as a heat source for the stripping process as a result.

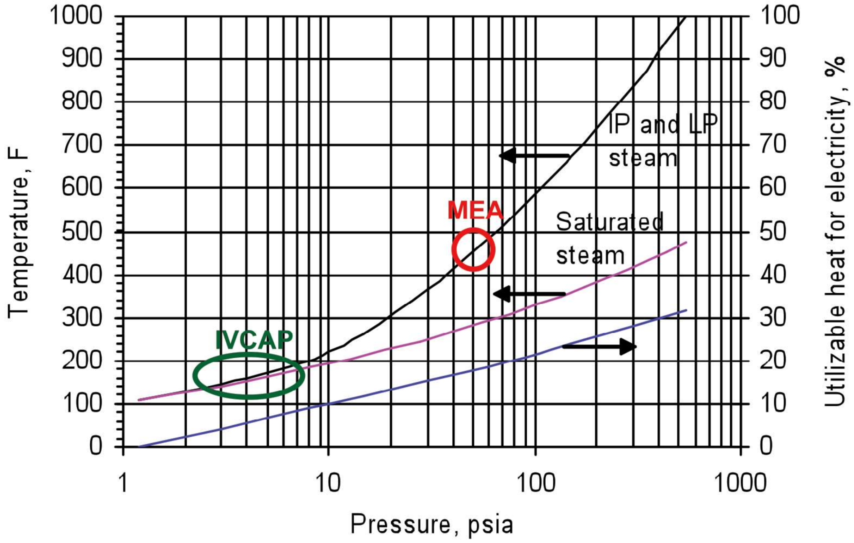

Figure 1: Steam Properties During Expansion in the Intermediate- and Low-Pressure Turbines

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Novel Integrated Vacuum Carbonate Process

participant:

Illinois State Geological Survey

project number:

NT0005498

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performance period:

10/1/08 – 4/30/12

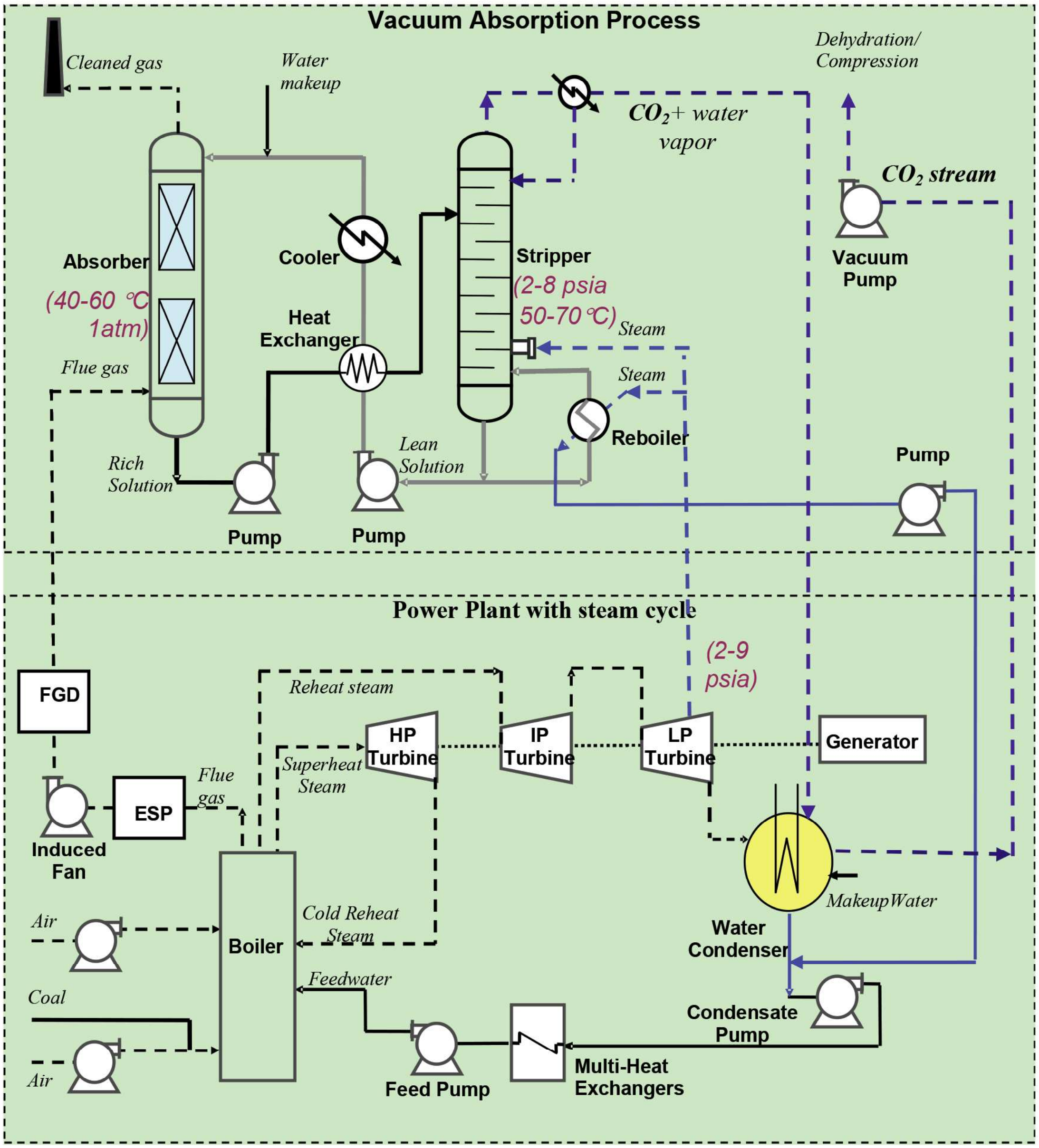

Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low-Quality Steam From the Power Plant

TABLE 1: A COMPARISON OF HEATS OF ABSORPTION FOR CO_2 SOLVENTS

Solvent	Main Reaction	Heat of Absorption
Primary/Secondary Amines	$2RR'NH + CO_2 = RR'NCOO^- + RR'NH_2$+	MEA: 1,900 kJ/kg
Tertiary Amine	$RR'R''N + CO_2 + H_2O = HCO_3^- + RR'R''NH^+$	MDEA: 1,200 kJ/kg
Carbonate	$CO_3$2- + CO_2 +H_2O = 2 HCO_3^-	600 kJ/kg

The intrinsic rate of CO_2 absorption into the K_2CO_3 solution is much slower than that in a monoethanolamine (MEA) solution; therefore, enzyme catalysts were developed to promote the absorption rate. Unlike the mixing of another solvent into a primary solvent, a catalyst accelerates the absorption rate without increasing the heat of absorption of the solvent.

The enzyme catalysts will need to be immobilized in order to:

- Reduce enzyme leakage in a flow system.
- Improve chemical stability of enzymes.
- Improve thermal stability of enzymes.

Three supportive matrices (i.e., carbon-, controlled pore glass [CPG]-, and silica-based materials) were evaluated for enzyme immobilization.

Since more than 60 to 70 percent of the process heat in the IVCAP is the stripping heat, an additive able to suppress water vaporization of the CO_2-loaded solution can reduce the stripping heat in the stripper. Successful screening and development of an additive can further reduce the heat use in the IVCAP.

The IVCAP has the flexibility to integrate SO_2 removal in the CO_2 capture process. In the amine-based and amine-promoted absorption processes, the flue gas must be treated to reduce the concentration of SO_2 and other acid gases to below 20 parts per million (ppm) to prevent/minimize the formation of heat-stable salts that are difficult to reclaim. In the IVCAP, SO_2 can be removed by the reaction with the solvent to form a sulfate salt that can be further processed to reclaim the solvent.

TABLE 2: PROCESS PARAMETERS FOR IVCAP PROCESS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	138	N/A
Normal Boiling Point	°C	103	N/A
Normal Freezing Point	°C	≤0	N/A
Vapor Pressure @ 15°C	bar	Not volatile	N/A
Manufacturing Cost for Solvent	$/kg	0.4-1.0	≤0.8
Working Solution			
Concentration	kg/kg	0.2	0.2
Specific Gravity (15°C/15°C)	-	1.24	N/A
Specific Heat Capacity @ STP	kJ/kg-K	3.34	N/A
Viscosity @ STP	cP	1.9	N/A
Absorption (Rich Solution at Bottom)			
Pressure	bar	0.06-0.08 (0.8-1.2 psia)	<0.1
Temperature	°C	40-60	40-60
Equilibrium CO_2 Loading	mol/mol	0.5	0.5
Heat of Absorption	kJ/mol CO_2	600	N/A
Solution Viscosity	cP	0.95 (at 50°C)	N/A
Desorption (Lean Solution at Bottom)			
Pressure (CO_2 equilibrium pressure)	bar	0.007-0.02 (0.1-0.3 psia)	≥0.01
Temperature	°C	50-70	50-70
Equilibrium CO_2 Loading	mol/mol	0.12-0.20	≤0.2
Heat of Desorption	kJ/mol CO_2	600	N/A
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	500,000 (100,000 kg/hr CO_2)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 99%, 0.14–0.54 (prior to vacuum pump)	
Adsorber Pressure Drop	bar	0.04 (structured packing)	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The main reactions involving in the IVCAP include:

CO_2 absorption: $CO_2+H_2O^+K_2CO_3 = 2KHCO_3$
Solvent regeneration: $2KHCO_3=K_2CO_3+H_2O^+CO_2$

Solvent Contaminant Resistance – Since the potassium carbonate solution is used as a solvent, no solvent degradation and little corrosion problems are expected. The $K_2CO_3/KHCO_3$ solution reacts with the flue gas contaminants (e.g., SO_2, nitrogen oxides [NO_x], hydrogen chloride [HCl], etc.). No SO_2 scrubbing pretreatment is needed prior to the IVCAP, since SO_2 removal can be combined with CO_2 capture and the potassium sulfate desulfurization product can be potentially reclaimed in the IVCAP.

Solvent Foaming Tendency – The $K_2CO_3/KHCO_3$ solution itself does not have a foaming problem. The addition of a carbonic anhydrase (CA) enzyme biocatalyst in the $K_2CO_3/KHCO_3$ solution will not incur a foaming tendency due to its low dosage (<3 g/l) and low contents of impurities.

Flue Gas Pretreatment Requirements – Sulfur dioxide removal can be combined with CO_2 capture in the IVCAP. The carbonate solution absorbs SO_2 to form a sulfate salt, which is reclaimable using a reclamation approach developed in this project. Therefore, a separate flue gas desulfurization (FGD) unit currently required in the power plant can be potentially downsized or even eliminated in the IVCAP. No other flue gas pretreatments (such as for particulate matter [PM], NO_x) are required either.

Solvent Make-Up Requirements – A thermophilic CA enzyme tested in the project demonstrated to be stable at 40°C. At 50°C, the enzyme had a half-life of approximately two months. After immobilization, the thermal stability of the enzyme has been significantly improved. The enzyme also demonstrated excellent chemical stability against the most abundant flue gas impurities. It is estimated that two to three replacements of the enzyme is required annually if the absorption operates at 50°C and 30 percent replacements is required at 40°C.

Waste Streams Generated – Waste streams mainly include the process blowdown streams, such as the carbonate/bicarbonate aqueous solution from the absorber/stripper and water condensate saturated with CO_2.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Uses lower-quality steam than amine-based processes (e.g., MEA), consequently increasing net power output.
- Lower heat of absorption.
- Less energy required for CO_2 stripping.
- Modified IVCAP may be able to remove SO_2 without an FGD unit.
- Approximately 25 percent lower electricity loss.

R&D challenges

- Slow kinetics of CO_2 absorption into the K_2CO_3 solution; thus, a high-activity catalyst is required.
- Potentially large capital and operating cost of the vacuum pump and vacuum stripper.
- Suppressing water vaporization in the stripper.
- Chemical and thermal stability of the absorption enzymes.

results to date/accomplishments

- Reactivity tests of two CA enzymes (ACA1 and ACA2) from a leading enzyme manufacturer and eight inorganic and organic catalysts commercially available were evaluated in a laboratory-stirred tank reactor (STR). The CA enzymes were identified to be the most-effective catalyst for promoting CO_2 absorption into $K_2CO_3/KHCO_3$ solution.
- Rates of CO_2 absorption into a 20 wt% $K_2CO_3/KHCO_3$ solution were increased by approximately three to nine times at temperatures between 25 and 50°C with the addition of 300 mg/l CA enzyme. Further increase in absorption rate was observed at higher CA concentrations (>300 mg/l CA). Absorption rates into CO_2-rich $K_2CO_3/KHCO_3$ solutions were comparable to those into CO_2-lean $K_2CO_3/KHCO_3$ solutions at the same CA dosage. Modeling predictions suggested that in a packed-bed column configuration, the IVCAP absorber at 2 g/l CA dosage was 23 to 40 percent larger than the equivalent equipment for the MEA process employing 5M MEA as a solvent.
- The CA enzymes demonstrated excellent chemical stability to resist flue gas impurities. Presence of flue gas impurities at their typical concentrations resulted in <11 percent loss of initial CA activity.
- The ACA1 enzyme had satisfactory stability at 25°C, but not at temperatures higher than 40°C. The ACA2 enzyme (a thermophilic CA) demonstrated excellent thermal stability at 40°C, losing only about 15 percent of its initial activity after six months. At 50°C, the ACA2 enzyme had a half-life of about two months.
- Covalent bonding methods were successfully developed to immobilize the CA enzymes onto different carbon-, CPG-, and silica-based support materials. All of the immobilized CA enzymes exhibited significantly improved thermal stability.
- Process simulation studies showed that the IVCAP integrated with a 528 MWe (gross) coal-fired, subcritical power plant at a baseline condition lowered parasitic power losses by 24 percent compared to the conventional MEA process.

- Techno-economic studies showed that the capital cost of the baseline IVCAP was about 33 percent higher than that for the MEA process due to the requirements for a vacuum pump and a larger stripper under a vacuum condition, but its operation and maintenance (O&M) cost was about 40 percent lower due to its lower solvent cost and reduced parasitic power losses. The levelized cost of electricity (LCOE, about $46/MWh) of the baseline IVCAP was a 71 percent increase over the reference power plant without CO_2 capture, about 17 percent less than that of the MEA process.

next steps

This project ended on April 30, 2012.

available reports/technical papers/presentations

Zhang, S., et. al, “Catalytic Behavior of Carbonic Anhydrase Enzyme Immobilized onto Nonporous Silica Nanoparticles for Enhancing CO_2 Absorption into a Carbonate Solution,” Int. J. Greenhouse Gas Control 2013, 13: 17-25.

Lu, Y., et. al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” Final Project Closeout Review, Pittsburgh, Pennsylvania, July 13, 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/IVCAP-Closeout-Mtg-0713.pdf*.

Lu, Y., et al, “An Integrated Vacuum Carbonate Absorption Process Enabled with an Enzyme Biocatalyst for CO_2 Absorption,” proceedings of the Clearwater Clean Coal Conference, Tampa, Florida, June 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Clearwater-IVCAP-YLu.pdf*.

Zhang S., et. al, “Activity and Stability of Immobilized Carbonic Anhydrase for Promoting CO_2 Absorption into A Carbonate Solution for Post-Combustion CO_2 Capture,” Bioresources Technology 2011, 102(22): 10194-10201.

Lu, Y., et. al, “Development of a Carbonate Absorption-Based Process for Post-Combustion CO_2 Capture: The Role of Biocatalyst to Promote CO_2 Absorption Rate,” Energy Procedia 2011, 4: 1286-1293.

Lu, Y., et. al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011.

Lu, Y., et.al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010.

Lu, Y., “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.