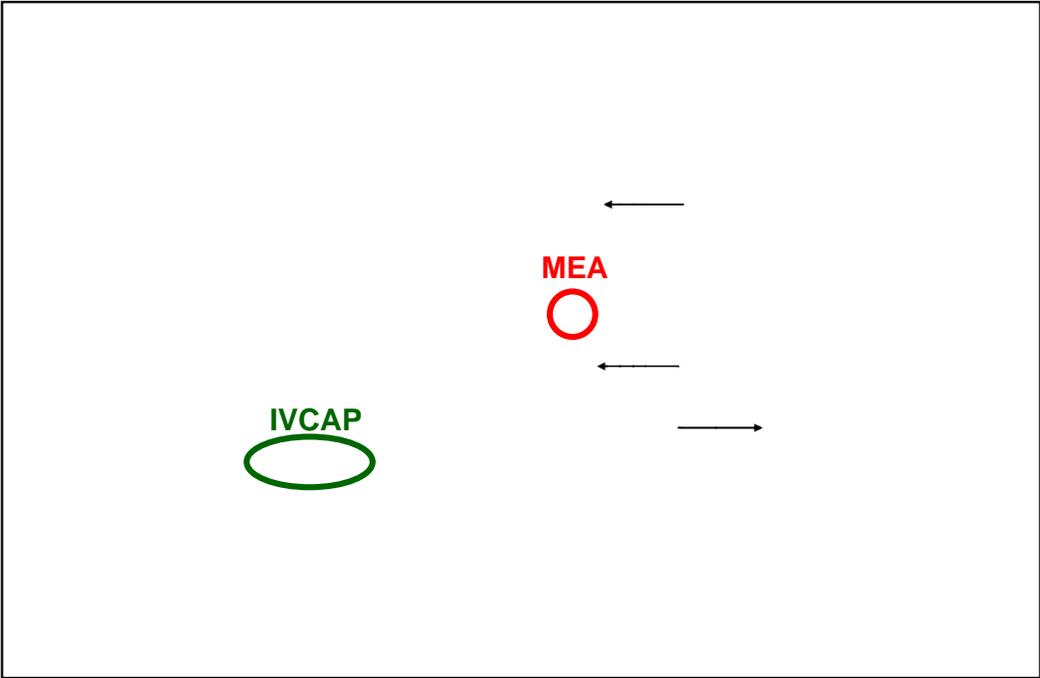


Project Title: Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process	
Technology Area: Post-Combustion Solvent	Technology Maturity: Laboratory-Scale, Simulated Flue Gas
Primary Project Goal: To prove the novel Integrated Vacuum Carbonate Absorption Process (IVCAP) concept and further improve the energy efficiency of the process for post-combustion carbon dioxide (CO ₂) capture.	
Technical Goals: <ul style="list-style-type: none"> • Test the proof-of-concept of the IVCAP. • Identify an effective catalyst for accelerating CO₂ absorption. • Identify an effective additive for reducing the stripping heat. • Evaluate a modified IVCAP as a multi-pollutant control process for combined sulfur dioxide (SO₂) and CO₂ capture. 	
Technical Content: The proposed IVCAP employs a potassium carbonate (K ₂ CO 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 ₂ CO 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	

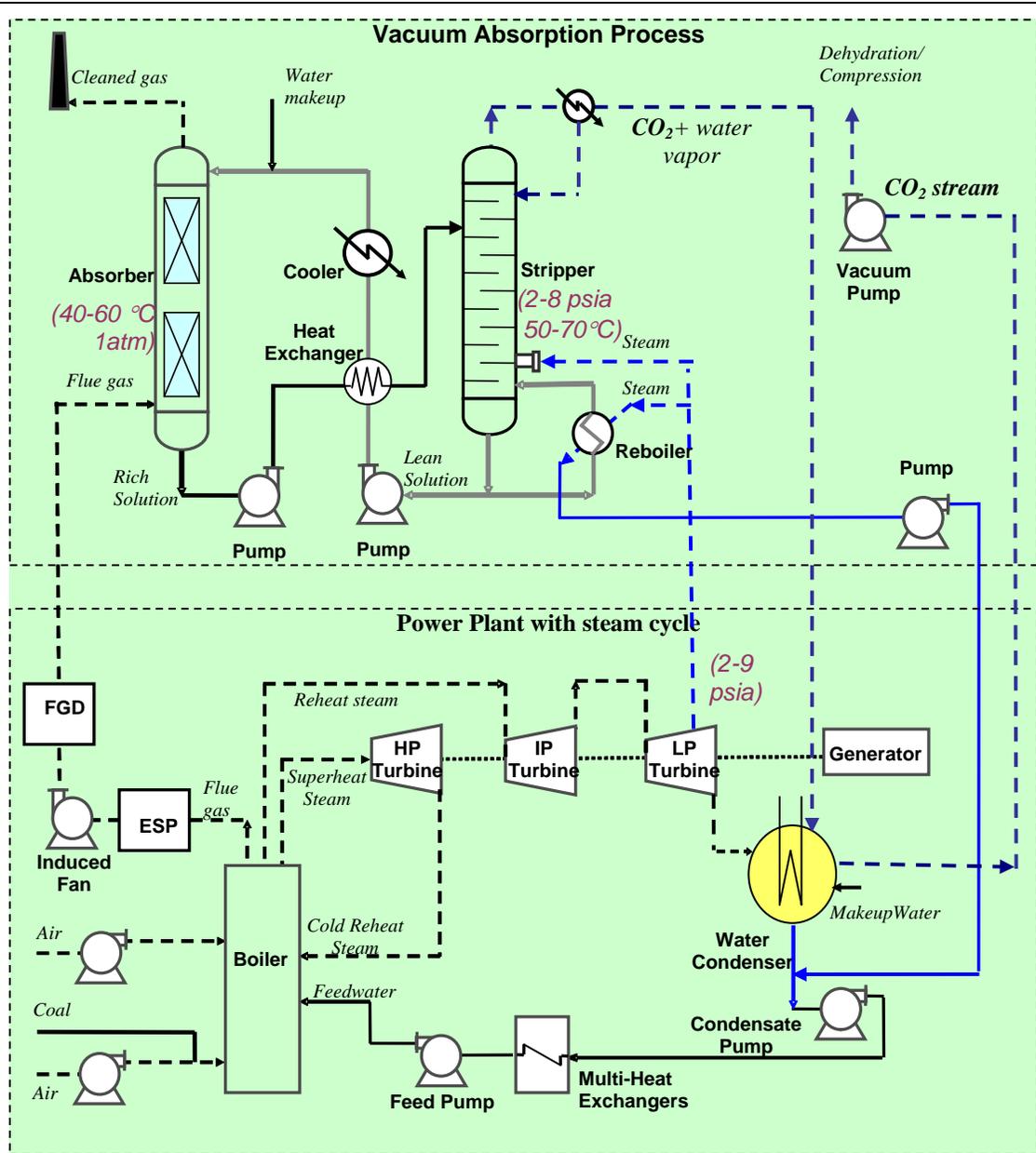


Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low Quality Steam From the Power Plant

Table 1: A Comparison of Heats of Absorption for CO₂ 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 CO₂ absorption into the K₂CO₃ solution is much slower in an MEA solution; therefore, enzyme catalysts will be 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-, ceramic- and polymer-based materials) will be evaluated for enzyme immobilization.

Since more than 60% of the process heat in the IVCAP is the stripping heat, an additive able to suppress water vaporization of the CO₂-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 SO₂ removal in the CO₂ capture process. In the amine-based and amine-promoted absorption processes, the flue gas must be treated to reduce the concentration of SO₂ and other acid gases to below 20 ppm to prevent/minimize the formation of heat-stable salts that are difficult to reclaim. In the IVCAP, SO₂ can be removed by the reaction with the solvent to form a sulfate salt which can be further processed to reclaim the solvent.

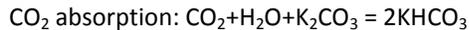
Process Parameters for IVCAP Process

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	K ₂ CO ₃ /KHCO ₃	
	Molecular weight	138	
	Boiling point (°C)	103	
	Heat of reaction (kJ/mole CO ₂)	26.4	
	CO ₂ loading/working capacity*, wt.%	2.7-4.0%wt	
	Solvent concentration to stripper (mol/liter)	20-25%wt	
	Heat capacity of solution (kJ/K/kg)	3.35	
	Viscosity, cP	0.95 (50°C)	
Operating Conditions	Absorption temperature, °C	40-60	
	Absorption pressure, atm.	1	
	CO ₂ capture efficiency, %	90%	
	Regeneration method	Pressure swing	
	Regeneration temperature, °C	50-70	
	Regeneration pressure, atm.	0.14-0.54	
Heat Integration	Required regeneration steam temperature, °C	60-100	
Miscellaneous	Solvent make-up rate, kg/kgCO ₂	negligible	
Product Quality (based on process simulations)	CO ₂ purity, %	>99	
	N ₂ concentration, %	negligible	
	Other contaminants, %	0.1%	
Process Performance	Electricity requirement, kJ/kgCO ₂ (compress. incl.)	460-580	
	Heat requirement, kJ/kgCO ₂	240-550 (Elec. equiv.)	
	Total energy (electricity equivalent), kJ/kgCO ₂	800-1130	~800

*Working capacity is the loading difference CO₂-rich solution before and after it is regenerated.

Equation/s describing chemical reaction:

The main reactions involving in the IVCAP include:



Solvent reaction kinetics:

Based on the experimental results to date, the overall CO₂ absorption rate measured for a 20%wt potassium carbonate (PC) solution mixed with 300 mg/l free carbonic anhydrase (CA) enzyme was about 1.5 to five times lower than that of the MEA, depending on the CO₂ loading in the solution. The CA enzyme promotes the absorption more significantly when the CO₂ loading in the solution is higher. The CO₂ absorption rate into the CA-promoted PC solution can be close to the MEA if a higher enzyme dosage level (>300 mg/l), an additive to increase CO₂ solubility in the solution, and an absorber configuration with large liquid holdup are further employed.

Solvent heating/cooling method:

There are two process configurations for heating and cooling the carbonate solvent in the IVCAP. If the stripper is operated at close to 70°C, a heat exchanger is employed for exchanging heat between the CO₂-rich solution from the absorber and CO₂-lean solution from the stripper. If the stripping temperature is chosen at close to 50°C, the heat exchange between the rich and lean solution can be eliminated, and only a cooler (using cooling water as medium) is used to cool down the lean solution before it enters the absorber.

Solvent contaminant resistance:

Since the potassium carbonate solution is used as a solvent, no solvent degradation and little corrosion problems are expected. No SO₂ scrubbing is needed prior to the IVCAP, since SO₂ removal can be combined with CO₂ capture. Therefore, there is also no problem related to SO₂ contamination.

Flue gas pretreatment requirements

Sulfur dioxide removal can be combined with CO₂ capture in the IVCAP. The carbonate solution absorbs SO₂ 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 eliminated in the IVCAP. No other flue gas pretreatments (such as for particulate matter [PM], nitrogen oxides [NO_x]) are required either.

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 CO₂.

Technology Advantages:

- Uses lower quality steam than amines (MEA), consequently increasing net power output.
- Lower heat of absorption.
- Higher absorption capacity.
- Less energy required for stripping.
- Modified IVCAP may be able to remove SO₂ without a FGD unit.
- Approximately 25% lower electricity loss.

R&D Challenges:

- Slow kinetics of CO₂ absorption into the K₂CO₃ solution and thus a high-activity catalyst is required.
- Potentially large capital and operating cost of the vacuum pump.
- Suppressing water vaporization in the stripper.
- Chemical and thermal stability of the absorption enzymes.

<ul style="list-style-type: none"> • Materials need to be developed to immobilize the enzymes. 	
<p>Results To Date/Accomplishments:</p> <ul style="list-style-type: none"> • Completed the reactivity test of CA enzyme from a leading enzyme manufacturer and the evaluation of existing inorganic catalysts. The results showed that the CA is a promising catalyst for accelerating CO₂ absorption into the K₂CO₃ solution. Evaluation on CA enzymes from other sources and enzyme immobilization research is currently underway. 	
<p>Planned Activities:</p> <ul style="list-style-type: none"> • Investigate catalytic methods to enhance the CO₂ absorption rate in the K₂CO₃ solution. <ul style="list-style-type: none"> ○ Evaluate and optimize activity of enzyme catalysts. ○ Investigate enzyme immobilization. ○ Evaluate other potential catalysts. • Screen and develop additives for suppressing water vaporization in the stripper. <ul style="list-style-type: none"> ○ Measure vapor-liquid phase equilibrium for the CO₂-H₂O-K₂CO₃-KHCO₃ systems with and without additives at a temperature range of 25°C to 70°C. ○ Inorganic and organic additives to be examined. • Combine SO₂ removal in the CO₂ capture process. <ul style="list-style-type: none"> ○ Evaluate reclamation reagents. ○ Conduct parametric tests in the batch and semi-continuous lab systems. • Conduct techno-economic analysis of the IVCAP. 	
<p>Available Reports/Technical Papers/Presentations:</p> <p>Presentation at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, March 2009.</p> <p>Poster presentation at the Eighth Annual Conference on Carbon Capture & Sequestration, Pittsburgh, Pennsylvania, May 2009.</p> <p>Presentation at the 2009 AIChE Annual Meeting, Nashville, Tennessee. November 2009.</p>	
<p>Contract No.: DE-NT0005498</p>	<p>NETL Project Manager: Robert Patton Robert.Patton@NETL.DOE.GOV</p>
<p>Principal Investigator: Yongqi Lu Illinois State Geological Survey lu@isgs.illinois.edu</p>	<p>Partners: Calgon Carbon Corporation Illinois Clean Coal Institute University of Illinois</p>