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GHGT-12

## Pi-CO<sub>2</sub> Aqueous Post-Combustion CO<sub>2</sub> Capture: Proof of Concept through Thermodynamic, Hydrodynamic, and Gas-Lift Pump Modeling

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### Abstract

Partnering in Innovation, Inc. (Pi-Innovation) introduces an aqueous post-combustion carbon dioxide (CO<sub>2</sub>) capture system (Pi-CO<sub>2</sub>) that offers high market value by directly addressing the primary constraints limiting beneficial re-use markets (lowering parasitic energy costs, reducing delivered cost of capture, eliminating the need for special solvents, etc.). A highly experienced team has completed initial design, modeling, manufacturing verification, and financial analysis for commercial market entry. Coupled thermodynamic and thermal-hydraulic mass transfer modeling results fully support proof of concept. Pi-CO<sub>2</sub> has the potential to lower total cost and risk to levels sufficient to stimulate global demand for CO<sub>2</sub> from local industrial sources.

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*Keywords:* Carbon Capture; Enhanced Oil Recovery; EOR; Greenhouse Gas; GHG; Carbon Dioxide; CO<sub>2</sub>; Dissolved CO<sub>2</sub>; Industrial Emission

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## 1. Introduction

Partnering in Innovation, Inc. (Pi-Innovation) introduces Pi-CO<sub>2</sub>, a novel post-combustion aqueous-based carbon dioxide (CO<sub>2</sub>) capture system. Pi-CO<sub>2</sub> is a patented method that uses well known processes and standard components to offer post-combustion CO<sub>2</sub> capture with low parasitic energy, low delivered CO<sub>2</sub> product pricing for the enhanced oil recovery (EOR) market, and no hazardous degradation by-products.

Although the Pi-CO<sub>2</sub> system was initially designed for Enhanced Oil Recovery (EOR) applications, Pi-Innovation is also part of the CO<sub>2</sub>-DISSOLVED project team, funded by the ANR (French National Research Agency). The CO<sub>2</sub>-DISSOLVED project examines an integration of CO<sub>2</sub> capture, geothermal heat production, and local CO<sub>2</sub> storage for low to medium CO<sub>2</sub> concentration industrial emissions [1]. In separate papers [2, 3] we assess the feasibility of integrating the Pi-CO<sub>2</sub> technology as part of the CO<sub>2</sub>-DISSOLVED concept, exploring specific modeling results in the context of low emission concentrations.

After a short description of the general configuration of the system, this paper presents thermodynamic, hydrodynamic, and gas-lift pump modeling results demonstrating the viability of the Pi-CO<sub>2</sub> concept in the context of EOR applications.

## 2. Process description

The system uses water as a physical solvent for the capture of CO<sub>2</sub> from flue gas. The water is circulated through a closed loop absorber and pressure swing desorber that operate in a large diameter, deep, water filled shaft that is sealed on the bottom and sides. The shaft functions as a very deep tank to create a range of hydrostatic pressure; from atmospheric pressure to approximately 60 bar. The higher hydrostatic pressures support maximized CO<sub>2</sub> solubility in water, and lower pressures promote pressure swing desorption. Figure 1 and the following process step discussion illustrate the general configuration of the system.

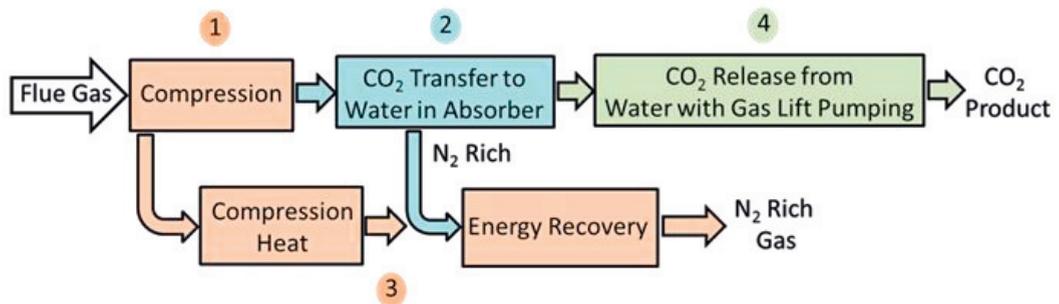


Figure 1 Generalized process steps for the Pi-CO<sub>2</sub> system

The primary process steps are as follows:

1. Flue gas is compressed and introduced into a counter-current absorber located in a sealed deep large diameter shaft (under 25 - 60 bar hydrostatic pressure).
2. Hydrostatic pressure significantly increases the solubility of gases in water; CO<sub>2</sub> is preferentially transferred to the water (physical solvent). The non-dissolved separated N<sub>2</sub> rich gas fraction is diverted to the surface.
3. Heat from compression is transferred to the pressurized N<sub>2</sub> rich gas stream from the absorber to recover compression energy with turbo-machinery.

- CO<sub>2</sub> effervesces from the water in the riser causing gas lift circulation to the surface, CO<sub>2</sub> is extracted, and water is returned to the tank; CO<sub>2</sub> product is compressed for delivery to the oil reservoir for enhanced oil recovery (EOR) via pipeline.

A simplified schematic of the configuration of the system in a large diameter deep shaft is shown in Figure 2. The figure shows the closed loop nature of the circulation, and the general position of the absorber and the riser pipe. The entry of compressed flue gas at approximately 60 bar (~600 meters depth), and the exit of the N<sub>2</sub> rich stream for heating and energy recovery are also shown on the diagram.

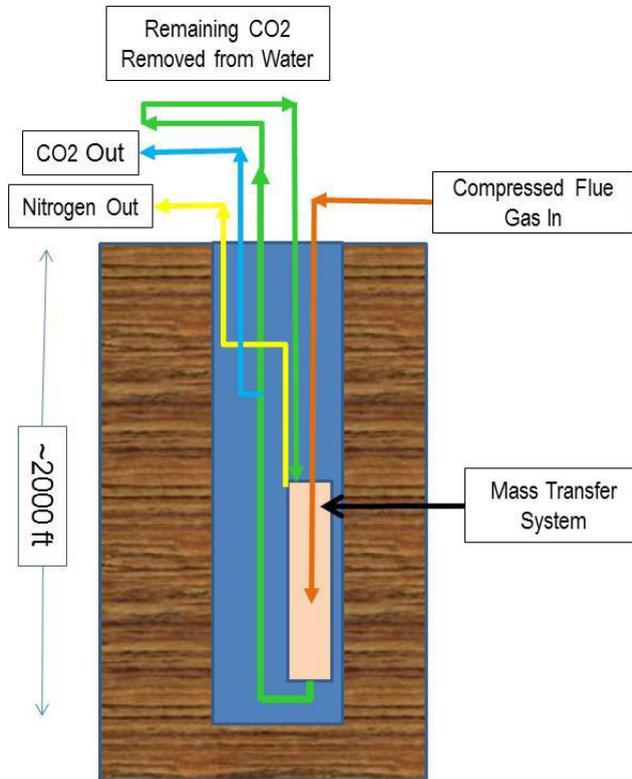


Figure 2 Simplified configuration of system

### 3. Process Modeling

The process was modeled with Aspen Plus<sup>TM</sup> to quantify energy consumers, heat transfer from compression to energy recovery, and energy producers. Energy consumers consist of flue gas compression and product compression, energy producers consist of expander turbines. The capture system is configured for energy conservation by linking consumers with producers. Pinch analysis was performed to for best use of the compression heat by expanders. The latest process flow of Pi-CO<sub>2</sub> includes integration of drive systems and additional energy recovery that further offset the energy and cost of CO<sub>2</sub> capture. Figure 3 is a simplified summary of an early version of the Pi-CO<sub>2</sub> process showing energy demand in megawatts electricity (MW<sub>e</sub>) for consumers and energy offsets by producers in MW<sub>e</sub> for a 100MWe coal fired power plant with 82.2 metric tons/hour captured (MT/hr). Cooling targets for intercoolers and after coolers for compression are also shown as low pressure (LP), medium pressure (MP), and high pressure steam (HP) as megawatts thermal energy (MW<sub>th</sub>). These cooling targets are for excess heat not recoverable by producers.

| 100-MW <sub>e</sub> (82.2-MT/hr CO <sub>2</sub> ) Coal-fired Power Plant Energy Summary |                       |   |                        |
|---|-----------------------|---|------------------------|
| <b>Power requirements:</b>  |                       |   |                        |
| <b>Consumers</b>  |                       | <b>Producers</b>                                      |                        |
| CO-01   | 33.63 MW <sub>e</sub> | TU-01   | 19.53 MW <sub>e</sub>  |
| CO-02A  | 6.01 MW <sub>e</sub>  | TU-02   | 20.64 MW <sub>e</sub>  |
| CO-02B  | 9.93 MW <sub>e</sub>  |   |                        |
| CO-02C  | 12.78 MW <sub>e</sub> |   |                        |
| PP-01   | 0.46 MW <sub>e</sub>  |   |                        |
| CO-03   | 10.01 MW <sub>e</sub> |   |                        |
|   |                       | Net work including CO <sub>2</sub> compression        | 32.64 MW <sub>e</sub>  |
|   |                       | Net work <i>excluding</i> CO <sub>2</sub> compression | 22.64 MW <sub>e</sub>  |
| <b>Heating requirements:</b>  |                       |   |                        |
|   |                       | Turbine preheat (recuperation only)                   | 0 MW <sub>th</sub>     |
| <b>Cooling targets:</b>   |                       |   |                        |
|   |                       | Air cooling to 45°C                                   | 33.76 MW <sub>th</sub> |
|   |                       | LP steam generation (125°C)                           | 3.781 MW <sub>th</sub> |
|   |                       | MP steam generation (175°C)                           | 4.200 MW <sub>th</sub> |
|   |                       | HP steam generation (250°C)                           | 1.941 MW <sub>th</sub> |

Figure 3 Early version of Pi-CO<sub>2</sub> energy summary for a hypothetical 100MWe coal fired power plant

#### 4. Mass Transfer Modeling

The transfer of CO<sub>2</sub> from the compressed flue gas to the water phase is performed in a patented multistage counter current cascading absorber that has an entry gas pressure of ~60bar. Figure 4 illustrates a simplified single absorber stage; showing water and flue gas entry and CO<sub>2</sub> enriched water and CO<sub>2</sub> depleted gas exit. The CO<sub>2</sub> depleted gas is directed down the absorber cascade. Houghton et al. [4] studied the transfer of CO<sub>2</sub> to water under pressure in bubble columns. The absorber throughput for the Pi-CO<sub>2</sub> system is far greater than most studies due to its large scale (diameter and length). Hills [5] investigated gas holdup behavior of bubble columns with high throughputs, and demonstrated that high gas velocities are achievable.

Drift flux modeling was used to evaluate the overall performance of the absorber for water velocity, void fraction, bubble diameter, bubble velocity, absorber dimensions, cascade attributes, water mass, CO<sub>2</sub> captured, and other parameters. A thermal-hydraulic drift-flux modeling approach is recognized in the literature as applicable for absorbers (Zuber and Findlay [6]; Wallis [7]; Lahey and Moody [8]; Collier [9]; Todreas and Kazimi [10]). Drift-flux modeling indicates that a single multistage cascading counter current absorber in a large diameter shaft is capable of capturing ~100 metric tons/hour CO<sub>2</sub> with greater than 90% capture efficiency. The system is scalable with the addition or removal of stages. Pi-CO<sub>2</sub> can be efficiently scaled to capture very high volumes of CO<sub>2</sub>.

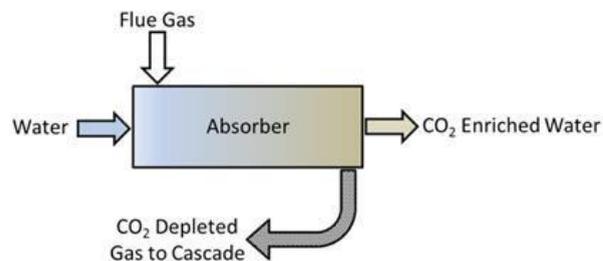


Figure 4 Simplified absorber diagram showing entries and exits

The step wise absorption of CO<sub>2</sub> in the stage and cascade operating line with comparison to equilibrium conditions is shown below (Figure 5). CO<sub>2</sub> concentration in the depleting flue gas is also illustrated with respect to the absorber cascade.

### Thermal Hydraulic Drift Flux Model

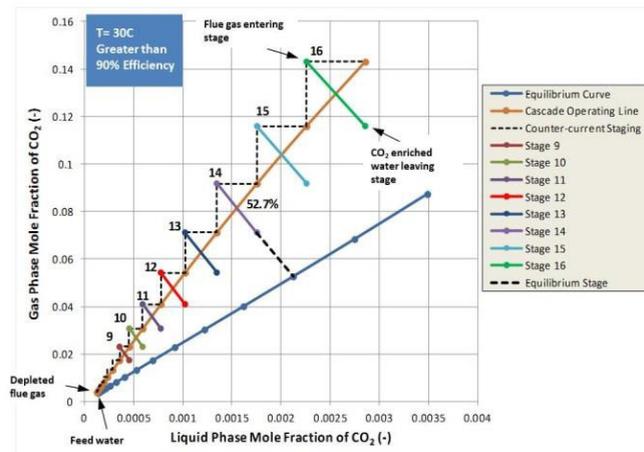


Figure 5 Modeled CO<sub>2</sub> absorption behavior in water using a multistage cascading absorber

### 5. Simple Gas-Lift Pumping Modeling

Water circulation in the Pi-CO<sub>2</sub> capture process is closed loop and uses gas-lift pumping to move the water. The compression energy of the gases that dissolve in the water provides the pumping energy through gas effervescence as the water rises up the return line in lower pressure conditions. The effervescing gas eliminates the need for a gas bubbler which is used in typical gas-lift pumping, and improves pump efficiency due to the uniform distribution of the effervescence.

Fan et. al. [11] performed a series of relatively large scale gas-lift pump tests in a freshwater lake in China. The tests were performed with a range of bubbler designs, they maintained relatively high gas flow rates, pumped large quantities of water, and maintained a high submergence factor. The general configuration of these tests is similar to pumping conditions for the Pi-CO<sub>2</sub> capture process except: 1) the scale is smaller in the test, 2) a bubbler was used, 3) the test system had relatively high pipe boundary effects, 4) the length of the riser pipe is shorter, 5) the Fan et al tests only operated under turbulent flow conditions. The highest pumping capacities are achieved under slug flow conditions common to gas lift pumps. Figure 6 is a graph showing a curve fit for some of the data derived by Fan et al. [11].

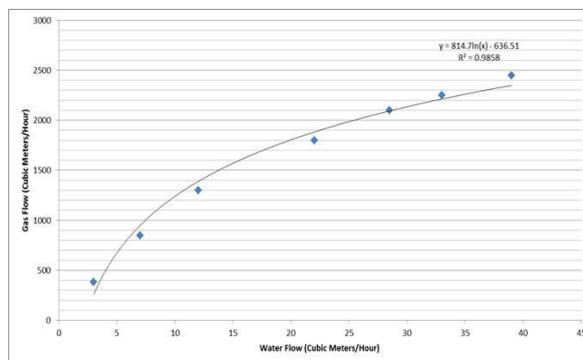


Figure 6 Fan et al.[11] data with natural log curve fit

When the empirical data from Fan et al. [11] is scaled for higher gas flow with the natural log curve ( $y=814.7\ln(x)-636.51$ ;  $R^2=0.98$ ) it is possible to generate a range of pumping capacities based upon metric tons of CO<sub>2</sub>/hour that would be effervescing from the water. Figure 7 is a graph of effervescing gas versus capacity of the pumped water to capture CO<sub>2</sub>.

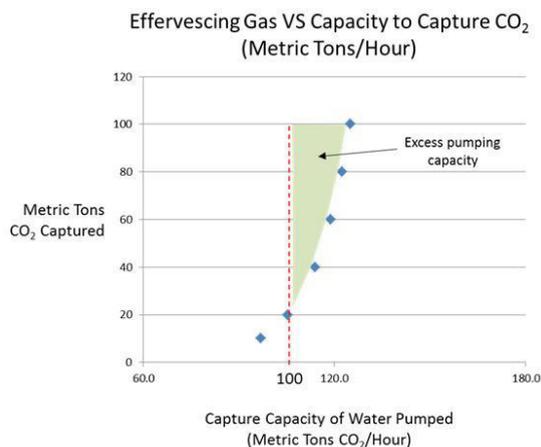


Figure 7 Effervescing gas versus capacity of the pumped water to capture CO<sub>2</sub>

The figure illustrates that a volume of 20 metric tons of effervescing CO<sub>2</sub> per hour can pump a water volume capable of capturing approximately 100 metric tons of CO<sub>2</sub> per hour. The efficiency of gas-lift pumps decrease when too much gas is introduced. This situation is illustrated in Figure 7 where the water pumping capacity for 100 metric tons per hour of effervescing CO<sub>2</sub> is only 125 metric tons per hour.

A simplistic gas-lift pump modeling using empirical data derived from large scale pump tests indicate that it is possible to circulate sufficient volumes of water for capture of over 100 mt/hr. The modeling effort also indicates that it will be necessary to remove the excessive gas effervescing from the rising water to maintain optimum gas-lift pumping that circulates water in the CO<sub>2</sub> capture system.

## 6. Conclusions

Process modeling with Aspen Plus<sup>TM</sup>, mass transfer modeling using a thermal-hydraulic drift-flux approach, and simple gas-lift modeling, indicates that a low total parasitic energy demand and high capture efficiency can be achieved with the Pi-CO<sub>2</sub> aqueous CO<sub>2</sub> capture system. The modeling also indicates that it is possible to construct a system with a capacity of approximately 100 metric tons per hour. Multiple shafts with cascading absorber systems and gas-lift pumping can be configured to achieve capture capacities compatible with CO<sub>2</sub> capture on a very large anthropogenic release scale. The large potential capture capacity is consistent with the size of the EOR market. Further modeling with the most current Pi-CO<sub>2</sub> design demonstrates that a high purity product of greater than 95% CO<sub>2</sub> can be produced. Financial analysis indicates that a CO<sub>2</sub> product can be captured, purified, compressed, and pipelined to reservoirs for EOR at a price equal to approximately 2.5% of crude oil value per 1000ft<sup>2</sup> CO<sub>2</sub> (crude oil at \$85/barrel).

Aspen Plus<sup>TM</sup> modeling of the system indicates that a product of greater than 95% CO<sub>2</sub> can be produced with a parasitic energy demand of less than 25% while recovering approximately 90% of the CO<sub>2</sub> from a coal based flue gas. The energy demand for system operation can be satisfied with a range of sources (electricity, steam, natural gas, process gas, etc.). Waste heat from a natural gas or process gas driven process can be recovered to significantly reduce overall energy cost.

Based on initial hydrodynamic modeling, mass transfer of CO<sub>2</sub> from the flue gas was shown to be feasible in a series of moderately sized absorbers. In coal combustion settings, detailed Drift Flux modeling of the patented Mass Transfer System (MTS) confirms that its unique configuration can provide high efficiency transfer of CO<sub>2</sub> to the water on a production scale.

This aqueous process is easily scalable using commercially available equipment for the aboveground components. Analysis of the gas-lift pumping capacity of the MTS indicates that the volumetric flow of off-gassing CO<sub>2</sub> is many times greater than that required to circulate the large volumes of water needed to achieve this production scale. Thus confirming gas lift pump efficiencies and confirming the assumption that additional energy and mechanical pumping are not needed for circulation.

The non-degradable nature of the physical solvent provides an opportunity to capture CO<sub>2</sub> from flue gases associated with coal combustion, refining, smelting, and cement manufacture. Desulfurization common to existing flue gas sources is required to limit the contact of sulfur with the water. Compression of the flue gas prior to entry into the MTS offers the opportunity to condense reduced mercury that would otherwise be released to the atmosphere. This offers a unique differentiator and additional positive cost-benefit for coal-fired power plant operations.

In summary, Pi-CO<sub>2</sub> uses well known processes and standard components in a novel configuration to offer CO<sub>2</sub> capture with low parasitic energy, low cost, no hazardous constituents, no greenhouse gas (GHG) solvent lifecycle costs, and multiple ancillary benefits. Modeling results fully support proof of concept and demonstrate excellent prediction for CO<sub>2</sub> and trace gas solubility; confirmation of energy demand and recovery potential; confirmation of step-wise mass transfer of the CO<sub>2</sub> into the water and ex-solution purification steps; gas lift pump efficiencies; maximized gas contact, retention time, and collection and discharge of non-dissolved gases for energy recovery; and achievement of equilibrium in the column with 90% recovery using the current system design.

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