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# CO2-Dissolved and Aqueous Gas Separation

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**Abstract**

Partnering in Innovation, Inc. (Pi-Innovation) offers a novel aqueous gas separation and carbon capture approach. Specific features in the design uniquely integrate multiple energy recovery processes and the potential for contaminant removal (i.e., oxides of sulphur (SOx), nitrogen (NOx), selenium (SeOx), and mercury (HgOx). CO2-DISSOLVED is an ANR multi-national project led by the BRGM, with Phase II funded as one of the first Geodenergies projects. Phase I explored the techno-economic feasibility of geothermal energy production combined with CO2 injection using a simplified version of the Pi-Innovation technology. Here we review the Pi-CO2capture process and the integration with dissolved injection applications.
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Peer-review under responsibility of the organizing committee of GHGT-13.
*Keywords:* Carbon Capture; Enhanced Oil Recovery; EOR; Greenhouse Gas; GHG; Geothermal Energy; Dissolved CO2; Post-Combustion

## 1. Introduction

CO2 Dissolved and Partnering in Innovation Inc. (Pi-Innovation) are collaborating to integrate aqueous CO2 storage with aqueous gas separation. Aqueous capture and storage of CO2 storage has applications including co-injection with reservoir flooding, with reproduced water in oil production, and in geothermal circulation systems. Pi-Innovation offers a patented aqueous gas separation and carbon capture technology that is highly promising in terms of potential total system cost reduction and energy recovery.

The CO2-Dissolved project evaluated the storage potential and techno-economic feasibility of co-injecting dissolved CO2 in a geothermal doublet in the Paris Basin.

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## 2. CO2-DISSOLVED

CO2-DISSOLVED is a multi-national project led by the Bureau de Recherches Géologiques et Minières (BRGM) and funded by the French National Research Agency (ANR) with Phase II funded as one of the first Geodenergies projects. Geodenergies is a French industry-driven initiative grouping 18 companies and research organizations aiming at: (1) structuring a community of expertise to promote subsurface energy technologies that are key to a global energy transition; (2) cross-fertilizing to develop 3 emerging industrial sectors: geothermal energy production,CO2 storage, and energy storage.

As the name "CO2-DISSOLVED" implies, the project focuses on the feasibility of the injection of dissolved CO2 in water, as opposed to supercritical CO2 injection. In this, and drawing from a process originally developed at a US Department of Energy (DOE) laboratory, Partnering in Innovation, Inc. (Pi-Innovation) offers a novel aqueous gas separation and carbon capture approach.

The CO2-Dissolved concept explores the storage of CO2 dissolved in water rather than in supercritical form; Kervévan et al. [1] and Kervévan et al. [2]. Figure 1 illustrates the carbonation of spent geothermal water in an injection well associated with a geothermal doublet Kervévan [3]. The dissolved form of CO2 storage in a saline aquifer is neutral to negatively buoyant, and shifts the geologic storage mechanism to the solubility trapping realm. Supercritical trapping relies on structural and stratigraphic trapping, and residual trapping, which is positively buoyant. Positive buoyancy represents a greater risk of uncontrolled release of CO2 to the surface. Figure 2 is a modification of the typical IPCC [4] geologic storage effectiveness diagram illustrating the range of CO2 trapping mechanisms versus storage security. Moving directly to solubility trapping offers lower brine displacement in the vicinity of the injection and significantly reduces the time required to achieve the highest level of geologic storage security.

The storage potential for CO2 in geothermal brine is limited by the solubility of the CO2 in the brine and the purity of the CO2 that is to be dissolved in the brine; due to gas competition in the dissolution process. This project targets low to medium range CO2 emitters (~10 to 150 kilotons/year) that could be compatible with a single doublet geothermal installation adjacent to the facility.

The coupling of geothermal heat with CO2 storage adds the potential for energy use and revenue generation, and adds the opportunity for valorization of the injection operations. In France, 650 potentially compatible industrial sites have been identified. These sites represent 25% of the stationary emissions for the country Kervévan [3].

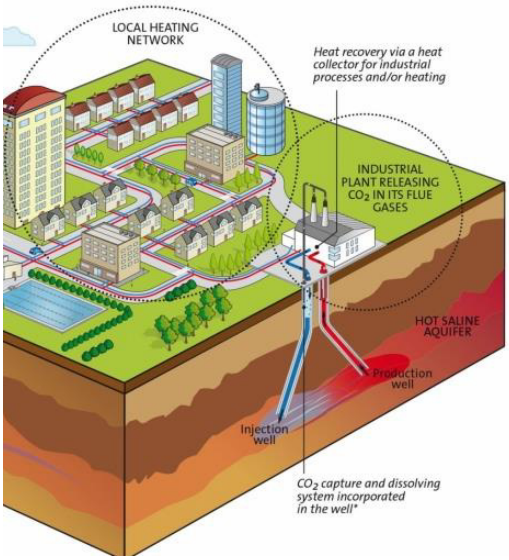


Figure 1 CO2-Dissolved: geothermal doublet injection well; Modified from BRGM, Kervévan [3]

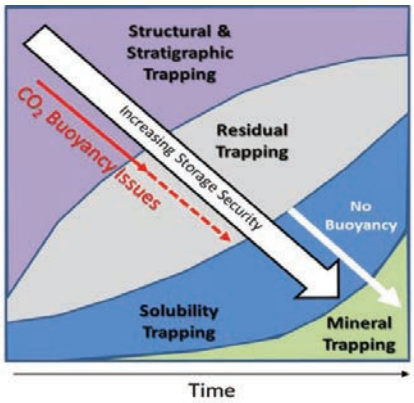


Figure 2 CO2 Trapping Mechanisms and Relative Storage Security Over Time

## 3. Pi-CO2

Partnering in Innovation Inc. offers post combustion CO2 capture using water as the physical mass transfer solvent. The patented Pi-CO2 process can be deployed on land or offshore, and has the capacity to remove SOx, NOx, and vaporized metals from the flue gas stream along with the CO2. The relatively complete treatment of flue gases adds the potential for substantial cost savings, providing capture incentives to a wide variety of flue gas sources typically containing moderately high CO2 contents (i.e., coal, cement, burnt lime, refining, smelting, biomass combustion, incineration, etc.).

The CO2 capture component of the process takes advantage of the solubility difference between CO2 and N2 in water at higher pressures and lower temperatures. Figure 3a illustrates the saturation concentrations of CO2 and N2 in water at 30 C, versus pressure. Figure 3b illustrates the saturation concentration of CO2 at various temperatures and pressures.

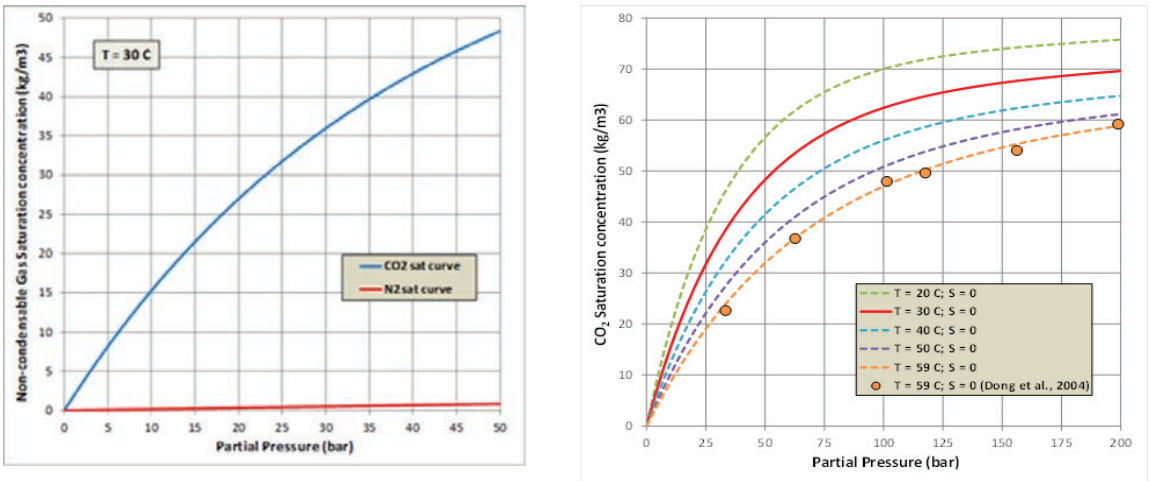


Figure 3a CO2 and N2 Saturation Concentration versus partial pressure at 30 C dissolved in pure water and 3b CO2 Solubility in pure water across a range of temperature and partial pressure conditions

Capture of CO2 occurs as water is circulated through a closed loop absorber and pressure swing desorber; the water in the closed loop is used "over and over again". High hydrostatic pressure magnifies the CO2 carrying capacity of the water. Lower temperature locations also further increased the CO2 carrying capacity. High hydrostatic pressure is achieved by placing the absorber/desorber in a water filled large diameter shaft, or through submergence in an offshore setting. Lower water temperatures can be acquired through submergence in relatively cold ocean or lake settings or by heat exchange with a natural cold water source.

The configuration of the absorber/desorber system is down-flow for the absorber and up-flow for the desorber. The absorber contains many stages that support sequential loading of CO2 into the water. Figure 4 shows the transfer of CO2 from the gas phase to the liquid phase in a down-flow absorber having 16 stages of mass transfer, operating at 30 C, with approximately 14% CO2 in the flue gas (similar to coal). The absorber will be more efficient with higher CO2 concentration emissions (i.e., cement, smelting and refining cat-crack), and less efficient at lower CO2 concentrations (i.e.,, natural gas fired turbines, natural gas fired power plants).

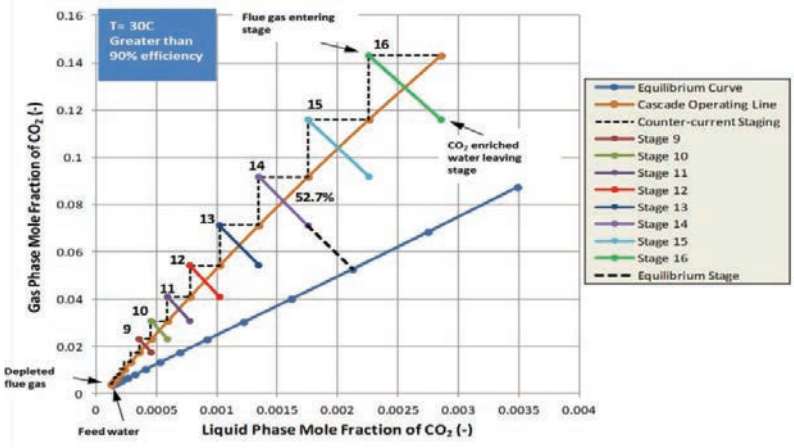


Figure 4 Step-wise CO2 transfer from the gas-phase to water-phase with a multi-stage down-flow cascading absorber.

The absorber efficiency will increase with: higher hydrostatic pressure, lower temperature, optimum bubble fraction, with longer absorber stages, and with an increase in the number of stages. The presence of free and dissolved N2 in the water in the absorber acts as a poison with respect to clathrate formation at the lowest conceivable temperature and highest conceivable pressure that the system is likely to be operated.

The desorber is configured to support sequential desorption promoting higher CO2 concentration in the final CO2 product and supporting gas lift pumping within the desorber. Gas lift pumping within the desorber drives the circulation within the absorber/desorber loop because the upward flow in the desorber achieves down-flow in the absorber.

Gas lift pumping is a well understood technology. However, most gas lift pumps are not typically on the scale of the Pi-CO2 process (diameter of the desorber riser and depth of submergence), and are not generally driven by effervescing gases (greater efficiency). Pump efficiency is controlled by the diameter of the rising pipe, bubble dispersion, gas volume, submergence ratio, and the height in which the pumped water is lifted; Awari et al. [5], Kassab et al. [6], and Barrut et al. [7]. The best performance in volume of water pumped can be achieved with: the largest diameter riser pipe, a high submergence ratio (submergence/lift height), an optimum volume of gas to make bubbles, and good bubble dispersion.

Fan et al. [8] performed a study of gas lift pumping with a relatively large diameter rising pipe, and relatively low water lift. Pi-Innovation developed a simple model using the empirical data derived from the study. A comparison with the modeling work of Fan et al. [8] suggests that there is more than sufficient gas to support pumping in the Pi-CO2 process. The challenge may be to selectively remove gas to maintain the optimum gas volume for optimum pumping in the desorber.

An important part of the Pi-CO2 process is the energy recovery from the pressurized non-dissolved gas that exits the top of the absorber. The process uses turbo-machinery to recover a large fraction of the compression energy penalty by combining the heat of compression with the pressurized gas. The Pi-CO2 process has similar parasitic energy requirements when compared to competing technologies (~22%) in a coal fired setting, but can take advantage of system waste heat for electricity production that offsets CO2 to an equivalency of 16 to 18%. The process can be driven by direct natural gas firing with alternate fuels, or driven with electricity. Direct firing can offer greater energy efficiency. The turbo-line can be electrically linked or mechanically linked as in some Compressed Air Energy Storage turbo-lines. Figure 5 shows a generalized sketch of the Pi-CO2 system.

Uniquely, the Pi-CO2 process removes SOx, NOx, vaporized metals, and CO2, in a single integrated process, The oxides are removed in compression condensate and at inter-cooler and after-cooler steps during flue gas compression. Figure 6 shows a simple chemical model output based upon Oxyfuel combustion flue gas compression empirical data, sourced from White et al. [9] and Huckaby [10].

SOx and NOx removal is usually required prior to CO2 capture because the presence of these compounds accelerates the degradation of typical capture chemicals (amines, sorbents, etc.); Rezaei and Jones [11], Supap et al. [12], Rohr et al. [13], and El Moudir [14]. Based upon CAPEX and OPEX costs from Cichanowitz [15], SOx pretreatment, alone, prior to CO2 capture, can add as much as $25 to $30 (US Dollars) to the cost of a metric ton of CO2 removed.

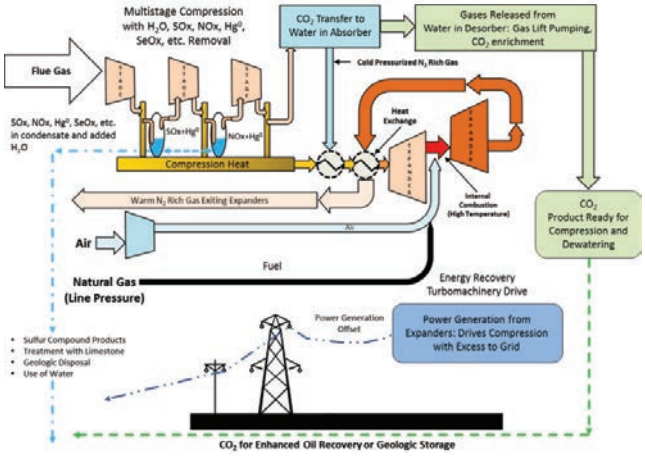


Figure 5 Generalized Pi-CO2 capture processes showing general energy recovery and flue gas contaminant removal

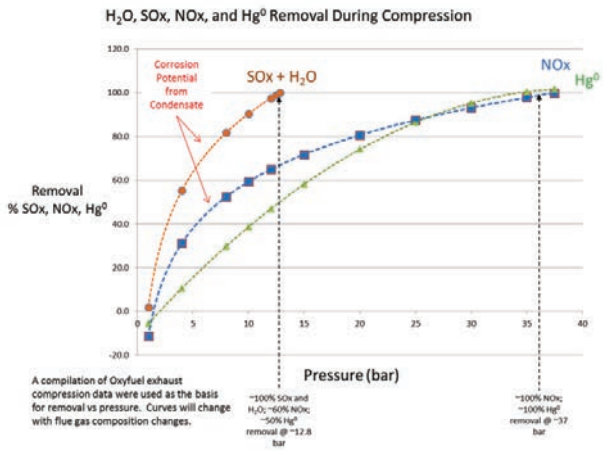


Figure 6 Simple chemical model output based upon empirical data from Oxyfuel flue gas compression studies.

The addition of heat to the turbo-line can allow for excess power generation to offset capital cost. Turbo-machinery is a very large part of the capital cost of the process. The potential to generate electricity is also useful because it can offset a portion of higher carbon sourced power on the grid in some locations which can improve the overall carbon reduction efficiency. Figure 7 illustrates this overall carbon reduction with electricity offset.

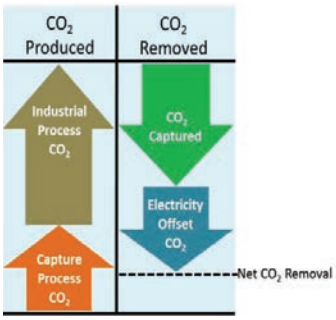


Figure 7 Overall carbon reduction with electricity offset

Energy demand is typically considered an important measure of operating cost between competing CO2 capture technologies. The Pi-CO2 process efficiently uses the power required for operation by recovering a large fraction of the compression energy penalty, using the energy of compression of the dissolved gas fraction to drive absorber/desorber pumping, and provides an opportunity to generate electricity offsets with the turbo-line.

CO2 capture with Pi-CO2 uses no expensive chemicals, has no significant chemical degradation, and no chemical wastes. The overall footprint of the technology is less because the absorber/desorber system is deployed in the subsurface or subsea. The capital cost can be lower when pretreatment for SOx, and NOx are considered, and future capital costs can be lower when Hg0 removal is considered. Operational costs are also low due to the use of long life turbomachinery for compression and energy recovery rather than chemical intensive processes.

## 4. Integration of CO2-DISSOLVED and Pi-CO2

The integration of aqueous CO2 storage with aqueous gas separation can offer lower risk geologic storage scenarios in situations where water is available for injection into saline aquifers. It is possible to capture CO2 from various industrial sources and produce a high purity CO2 product for use as supercritical CO2, or use relatively pure CO2 dissolved in water with the Pi-CO2 absorber technology, and directly inject the water into the subsurface. It is also possible to capture the CO2 from flue gas with the Pi-CO2 process absorber and inject the absorber discharge into the subsurface.

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