

CO₂/Brine Surface Dissolution and Injection: CO₂ Storage Enhancement

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Summary

Carbon capture and storage (CCS) is capable of reducing atmospheric emissions of greenhouse gases from coal or gas-fired power plants. The upward buoyancy of dense-phase carbon dioxide (CO₂) in deep reservoirs means that sites need to be chosen with a methodology that carefully evaluates details of performance during and after the injection process. Standard methods of site evaluation for saline aquifers overwhelmingly focus on the aspects of geological containment and monitorability. Also important to storage-site performance is the engineering design of transport and injection. Transport to storage in offshore saline aquifers is normally expected to be by pipeline. There are several proposed methods of CO₂ injection: for example, as a dense phase, in the liquid or supercritical phase, as water-alternating-gas cycles, or as carbonated brine. These result in different migration pathways in the aquifer during the short term (1 to 50 years) and different storage distributions in the long term (1,000 to 10,000 years). To develop a methodology suitable for making informed decisions for aquifers offshore of the UK, several of these different methods are being evaluated. A chemical-engineering and reservoir-engineering approach will be used to define some of the important surface-transport and subsurface interactions. Important surface features may include the energy balance, location, sizing, materials specification, and costing of surface equipment for mixing and transporting CO₂.

Introduction

Fossil-fuel combustion produces CO₂, which is a major greenhouse gas. Society now consumes approximately 13 TW (1 TW = 10¹², W = 3.2 EJ/year) of energy worldwide, and approximately 80% of that comes from burning fossil fuels (Goldemberg and Johansson 2004). Kaya (1995) suggests that there is a direct link between net CO₂ emissions (indicated by carbon *C*) and human population (*P*), economic development (indicated by the gross domestic product (*GDP*), energy production (*E*), and carbon-based fuels used for energy production (*F*). This was modified by Hoffert et al. (1998) to include CO₂ sinks (*S*_{CO₂}); hence, *C* is expressed

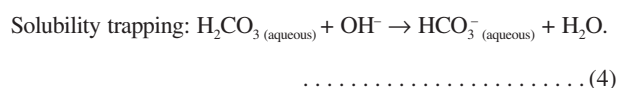
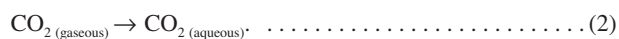
$$C = P \frac{GDP}{P} \frac{E}{GDP} \frac{F}{E} - S_{CO_2} \quad (1)$$

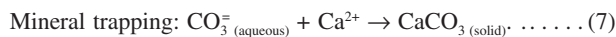
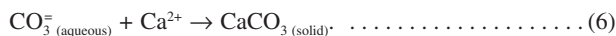
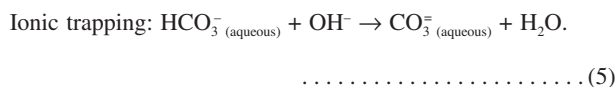
This relationship shows that the forces that drive the increase in anthropogenic CO₂ emissions are population increase, per capita *GDP* (also known as affluence level), the energy intensity of the economy (*E/GDP*), and the carbon intensity of the energy system (*F/E*). The term *E/GDP* reflects the sectorial makeup of the economy (i.e., how much energy-intensive industry is present), climate effects (i.e., how much heating and/or cooling is needed), and the energy efficiency of the economy (Bachu 2008). Fossil fuels will inevitably continue to be a major energy source for decades to come, as global population and energy demand is growing rapidly, particularly in developing economies such as China and India, with no absolute reduction in established emitters such as the USA or the EU. These huge fossil-fuel consumptions directly translate to massive CO₂ emissions and CCS and pose an important element

and require studies of various alternatives to enhance permanent CO₂ storage in deep geological formations.

CCS is widely recognized as an important option to reduce atmospheric CO₂ emissions. Specifically, CCS has the potential to provide emissions cuts sufficient to stabilize greenhouse-gas levels, while still allowing for the continued use of fossil fuels (Wilson et al. 2008). This can act as a transitional technology to buy time in which to improve the delivery of long-term low-carbon renewable generation. Storage methods currently attracting attention from the scientific community consist of injecting carbon dioxide into deep saline aquifers (Pruess and Garcia 2002), depleted abandoned hydrocarbon reservoirs, or unmineable coal seams. This project focuses solely on CO₂ storage in saline formations. Saline formations are deep sedimentary rocks saturated with formation waters or brines containing high concentrations of dissolved salts. These formations are widespread, and the water is unsuitable for agriculture or human consumption. The injection of CO₂ into deep saline formations is similar, in principle, to injection of water or CO₂ during hydrocarbon production into oil and gas fields. It is estimated that saline aquifers have the largest volume potential to store CO₂ worldwide. The International Energy Agency Greenhouse Gas Research and Development Programme (IEAGHG 1994) estimated in the early 1990s that the global potential for storage of CO₂ in deep saline reservoirs is between 400 and 10 000 Gtonnes of CO₂. Deep saline aquifers have the largest storage capacities among the geological storage options. Deep saline aquifers are present in most countries, and storage locations are not limited to hydrocarbon-bearing areas. Many saline formations are not extensively explored, characterized, or assessed for CO₂ storage. Geologic information about specific sites is more limited than for oil and gas fields, and these formations do not have the same assurance as in oil and gas reservoirs that there is a seal or a structure with closure capable of preventing the upward migration of CO₂. Injecting CO₂ could increase the migration of salty waters toward potable-water zones. If CO₂ leakage to the surface occurs, there is a potential for upward mobilization of heavy metals from deeper saline brine and contamination of drinking water. To reduce uncertainties, evaluation of saline formations using reservoir-modeling simulations is a useful first step, potentially followed by test drilling and injection. An enhanced ability to monitor and verify the behavior of geologically stored CO₂ may also be needed.

Geological CO₂ storage for long time scales (sequestration) relies on the contribution of several CO₂-trapping mechanisms: (1) the physical trapping of CO₂ in a gaseous, liquid, or critical state in a subsurface formation; (2) solubility trapping, which is the trapping of CO₂ by the dissolution of CO₂ within a brine, hydrocarbon, or other subsurface fluid; (3) hydrodynamic trapping, which is the residual saturation of disconnected CO₂ within individual pores, and (4) mineral trapping—the process of forming in-situ, interstitial carbonate minerals from CO₂ and the host rock and the formation waters (Hitchon 1996). Most of the trapping mechanisms are interconnected. The most basic chemical reactions that lead to solubility trapping and mineral carbonation are (Gunter et al. 2004) the following.





Although more-complex reactions may also take place with Ca- and Mg-rich minerals (Gunter et al. 2004; Gunter et al. 2000), subsurface mineralization is a slow long-term process that is strongly dependent on the availability of reactive minerals, such as Ca-rich feldspars, Mg/Fe-rich clays and micas, Fe-oxides or olivine (Hangx and Spiers 2009).

The technologies for capturing, transporting, and injecting CO₂ from industrial facilities draw upon a large body of existing research and field experience in the energy industry that are generally well understood (Gale and Kaya 2003; IPCC Working Group III 2005). CCS appears to be achievable from a technical perspective, although there are significant issues of scaleup and optimization of continuous and reliable processes. A number of important scientific uncertainties remain. Currently there are a wide range of scientific, technological, economic, safety, and regulatory issues connected to CCS, and there is a need for further research to address gaps in our knowledge. With respect to the sequestered CO₂, there are concerns about both its buoyancy and its migration underground, as well as the possibility of leakage and escape to the surface (IPCC Working Group III 2005). Surface releases would undermine efforts to stabilize atmospheric CO₂ concentrations and could, in a worst-case scenario, pose environmental and human-health risks (IPCC Working Group III 2005). Hence, continued reliance on fossil fuels in the face of global climate change requires pertinent collaboration between geoscientists, engineers, and other multidisciplinary professionals, both for the development of CCS technologies and to formulate strategies to eliminate certain risks associated with storage of large quantities of CO₂ permanently in geological formations. Risk in its engineering definition is the product of the likelihood of an event to occur and the consequences of the event taking place (Bachu 2008). The risks associated with CO₂ surface and injection facilities are well understood and documented (Damen et al. 2006).

Successful storage of CO₂ in the geological formations such as Utsira aquifer (for the Sleipner field) (Korbøl and Kaddour 1995) and enhanced oil recovery at Weyburn (Malik and Islam 2000) rely on an impermeable seal at the top of the formation to trap the fluid CO₂ (Jessen et al. 2005). This storage mechanism may be reliable in well-characterized sedimentary basins such as oil and gas fields where hydrocarbons have been trapped for geological time. However, ensuring perfect containment is more difficult in less-known aquifer formations with possible faulty seals or wells (Bruant et al. 2002; Bachu 2008) through which the CO₂ could leak to the surface. Assessment of uncertainties associated with the injection of CO₂ (for example, CO₂ leakage associated with pipeline or geologic formation failures) requires detailed study of various injection scenarios. This paper is part of an ongoing effort to develop a methodology for evaluation and monitoring of CO₂ aquifer storage sites. The paper focuses on investigation of various injection strategies, including those that do not rely entirely on an impermeable seal in an attempt to enhance long-term CO₂ storage and improve the reliability of storage. The study uses chemical-engineering processing operations to investigate some of the important surface-transport and subsurface interactions suitable to make informed choices for CO₂ aquifer storage sites in the UK. Four CCS injection strategies were proposed in an effort to give policymakers further information on potential CCS injection options. The conceptual designs of these methods consider the operational and phase behavior of CO₂ because it can cause considerable process concerns, particularly with respect to possible phase changes. Carbon dioxide at critical temperature and pressure (i.e., $T_c = 30.978^\circ\text{C}$, $P_c = 7.3773 \text{ MPa}$) has a density of approximately 467.6 kg/m³ (Span and Wagner 1996), which allows significantly greater quantities to be sequestered than if it existed in the gas

phase. Conditions that support the existence of supercritical CO₂ should be present at depths greater than 800 m corresponding to pressure and temperature above the critical point of CO₂. At pressures and temperatures above the critical point, CO₂ will exist in the dense-phase region (Hitchon 1996). The models described in this paper assume that the CO₂ stream used is dried or contains negligible water and is pressure boosted to achieve a dense-phase fluid for efficient pipeline transport to a storage site.

Injection Strategies: Materials, Software, and Design Considerations

The uncertainties associated with the underground geological formation are the fundamental concern and can be contrasted against the cost of improved CCS or injection technology that may be able to gain acceptance. Here, we study innovative concepts that could tackle these uncertainties and enhance CO₂ storage in the formations. Injection strategies investigated were standard CO₂ injection, CO₂/brine surface mixing and injection, CO₂/water surface mixing and injection, and CO₂-alternating-brine (CAB) injection strategy. A generic design and simulation of these strategies is presented, but the application to the two case scenarios involved in the project will be published later.

Proper study of these injection strategies requires simulation to provide information relating to the behavior of CO₂ in process facilities. The important predictions required were density of injected CO₂ relative to brine and density of CO₂/brine-saturated stream, CO₂/water-saturated stream, and other reservoir fluids (at surface and geological-formation pressure, temperature, and salinity); solubilities of CO₂ in brine and CO₂ in water; and associated phase diagrams. The injection-strategy surface-process-simulation models were constructed in Aspen HYSYS®, AspenTech's commercial simulation package. Schlumberger's PIPESIM® is used to model flow from the injection-wellhead facilities through into the reservoir, to address complex injection networks and capture the interactions between wells and process equipment and to perform a comprehensive sensitivity analysis at any point. This research project uses PIPESIM specifically for injection- and extraction-well design, as well as interfacing with other process packages (e.g., HYSYS), which is the next stage of this work. The software packages used for the modeling of chemical processes do place demands to ensure that sufficient equipment data, stream flows, compositions, and process operating conditions are supplied to render the model solvable. The commercial process simulators in practice deal with a problem that is often complex, involving large numbers of equations (linear and nonlinear) solved using relatively sophisticated techniques. The software packages are configurable and can model a wide range of chemical processes. In essence, process simulations are examples of the general class of models, which can be defined as a broad collection of methods used to study and analyze the behavior and performance of actual or theoretical systems. The model involves the solution of equations that describe the system being studied in order to derive information about that system. Typically, the process simulator constructed equations that describe various relationships such as energy balances, mass balances, vapor/liquid equilibria, calculated physical properties, and equipment performance. The injection-scenario models we propose in this paper were based on generic CCS processing. We have implemented a range of published algorithms in an in-house academic code in order to calculate subsurface densities of pure CO₂ (Huang et al. 1985) and pure water and brine (Danesh 2003), solubilities of CO₂ in pure water and brine (Spycher et al. 2003; Spycher and Pruess 2005), and CO₂-saturated fluid densities (García 2001).

Transmission, injection, and storage of a large CO₂ stream is a challenge for engineers, and there are many considerations to be made. There are four basic components to a supercritical CO₂-subsurface-injection scheme. These are (1) capture, (2) compression, (3) transport, and (4) injection. The main CO₂-injection facilities are the compression unit (if not already compressed at the captured source), the pipeline, the pumps, the injection wellhead, and downhole and monitoring equipment. This paper will address

Components 1 and 2 peripherally but will focus on Components 3 and 4. The reservoir-engineering aspects of CO₂ injection will not be covered in detail, but we consider the process from compression station to the bottom of the injection well. A detailed compression scheme will not be presented, but the final compressed-CO₂ pressure should be equal to wellhead pressure at the injection well.

The CO₂ capture/compressor station, surface mixing equipment, and injection facilities should be installed as near as possible to the injection wellhead to minimize pipeline expense. CO₂ pipelines are similar to natural-gas pipelines, and they can transport CO₂ from its source to a sink. The primary difference between CO₂ and natural-gas pipelines is that CO₂ pipelines require careful handling to keep the CO₂ stream in supercritical state. Design and operation of CO₂ pipelines require comprehensive understanding of the dynamic effects of flow. Dedicated CO₂ pipelines are currently used for EOR in the Permian Basin in the Weyburn oil field and at Snohvit, offshore Norway. In the Kinder Morgan pipeline, which services the Permian Basin, 1 Bcf/D of dry CO₂ is compressed to between 900 to 2,000 psi and transported 500 miles (Kinder Morgan 2010). Adapting this knowledge, power stations will dry CO₂ streams to the level required to prevent hydrate formation/internal corrosion and then compress and inject it into pipelines. Over long pipeline distances, booster stations will periodically recompress the CO₂. The design of the pipeline essentially follows conventional methods. The pipeline should be coated with external coating to prevent soil moisture from damaging the steel. Material specification and pipeline operation should consider occurrence of low temperatures under normal operating conditions or during depressurization. Special CO₂-resistant materials, such as nylon and viton, are considered to be appropriate for use in valves, control seals, and packing. Pressure piping is usually specified by nominal pipe size (NPS) and schedule (SCH). Pipe sizes are documented by a number of standards, including API 5L, ANSI/ASME B36.10M in the US and BS 1600, BS 1387, and BS EN 10255 in the UK and Europe. The manufacture and installation of pressure piping is tightly regulated by the ASME B31 code series such as B31.1 or B31.3, which have their basis in the ASME Boiler and Pressure Vessel Code. It is normally assumed that the injected-CO₂ stream will not contain any free water and will be injected as a single phase. Theoretically, carbon steel could be used for pipeline construction because of the low water content of the supercritical CO₂. However, some injection strategies investigated here, such as CO₂/brine surface mixing and CO₂-water surface mixing, require mixing of the supercritical CO₂ stream with brine or water and dehydration is not possible. These strategies involve handling of wet CO₂ (e.g., containing free water) with high corrosion potential and therefore are not applicable to carbon-steel pipes. Cosham and Eiber (2007) suggest inhibitor addition in carbon-steel pipes if dehydration is not possible. However, considering suitable material and public safety, which is of paramount importance, the 304/316L stainless-steel pipeline should be employed for best corrosion resistance in the injection manifold/station. All other downstream piping, vessels, and other equipment should be constructed with stainless steel. This is a high-performance option, but is costly.

The injection pump is designed to increase the pressure of the CO₂ to the required injection conditions. The pipeline around injection facilities is selected on the basis of the results from the pressure-drop calculations and should be constructed with stainless steel. Details of injection- and extraction-well design are not presented. Pressure gauges are installed both on the wellhead and downhole to observe the pressure development in the reservoir. The pressure gauges also monitor the change in density in the hydrostatic CO₂ column because of a shift in temperature during injection. The CO₂ pump and wellhead pressure are expected to be a function of CO₂-injection rate at initial reservoir pressure and at formation-fracture pressure.

Model Construction

The injection-strategy process-simulation models were created with the following input: process input data (flows, compositions, and process operating conditions), thermodynamic package [Peng

Robinson (PR), Soave Redlich Kwong (SRK)], process flow diagram (pieces of equipment are connected together), and process equipment data (pipeline profile, pump-compressor-performance curves or efficiency). The models were constructed with the least equipment possible while adequately modeling the process.

Generally, the simulations were used to determine how the streams entering the process behave (such as stream enthalpies and equipment performances) and to ensure that the flow regime of products exiting the process in this case remains in single phase (liquid only/dense phase). Considering the generic case for the injection-strategy models, the stream conditions and properties used (Table 1) are the same. HYSYS performs rigorous mass and energy balances of each injection process on the basis of the equation of state (Peng and Robinson 1976) selected. Descriptions of the constructed injection-strategy models are presented.

Phase Behavior

The first step in calculating any injection scenarios is the calculation of the phase envelope. A good understanding of fluid phase behavior is very important in the design of the CO₂-injection process. The intersection of injection profile and phase envelope can have a dramatic effect and can produce discrete gas or multiple liquids. The stream composition, phase behavior, and physical properties were important in all aspects of the injection methods. The simulations employ an equation-of-state package that treats a multicomponent system. Chemical reactions between CO₂ and rock minerals that could potentially contribute to mineral trapping of CO₂ are not covered. There are a number of thermodynamic packages available in the HYSYS commercial simulator, which incorporates various equations of state. Equations of state describe how a fluid will behave thermodynamically. In all process cases presented, unless otherwise stated, the properties were calculated using the Peng and Robinson (1976) equation of state, which provides an accurate reflection of the behavior of streams.

We calculated and constantly monitored the CO₂ stream properties in the facilities such as temperature, pressure (Figs. 1 and 2), enthalpy (Fig. 3), and other thermodynamic properties of the CO₂ stream in the process facilities to ensure the stream remains in supercritical state at all times. A small impurity (approximately 5%) in the captured CO₂ stream has huge negative impact in the phase behavior of the stream and imposes major operational problems in the process facilities. As shown in Fig. 1 with a pure CO₂ stream and Fig. 2 for CO₂ stream with 5% impurities, operating at conditions below critical point is problematic and should be avoided.

Subsurface Properties

We have investigated the subsurface phase solubility and densities of materials relevant to this study (Fig. 4). Specifically pure CO₂, fresh water, brine with constant composition, CO₂-saturated fresh water, and CO₂-saturated brine. The basic subsurface modeling was performed using an academic code generated within our group using R and validated against published data. The modeling does not perform a dynamic reservoir simulation; it returns material properties if the injection were to exist in an isolated form at subsurface pressure and temperature conditions. The value of this approach is to identify key initial conditions at different depths for which a reservoir simulation is overkill, and the coupled processes will be exploited in a full reservoir simulation. This represents a good first-order approximation from which further work should be informed. The inputs to this modeling are pressure and temperature surface values and gradients (used to calculate downhole pressure and temperature pairs) and the brine composition. The density of pure CO₂ was calculated using that method of Huang et al. (1985). The density of the pure water and brine were calculated following Danesh (2003). The solubilities of CO₂ in pure water and brine were calculated using Spycher and Pruess (2005) and Spycher et al. (2003). The CO₂-saturated densities were calculated using the pure densities corrected using the partial molar volume, as described by García (2001).

We used atmospheric surface pressure with a pressure gradient of 10 MPa/km and a surface temperature of 10°C with a

TABLE 1—CO ₂ STREAM CONDITIONS AND PROPERTIES*		
	Conditions	
	Overall	Liquid Phase
Vapor/Phase fraction	0.0000*	1.0000
Temperature (C)	30.50	30.50
Pressure (kPa)	1.800e+004*	1.800e+004
Molar flow (kgmole/h)	1.849e+004*	1.849e+004
Mass flow (kg/h)	8.142e+005	8.142e+005
Std ideal liq vol flow (m ³ /h)	1048	1048
Molar enthalpy (kJ/kgmole)	-3.950e+005	-3.950e+005
Molar entropy (kJ/kgmole-C)	103.2	103.2
Heat flow (kJ/h)	-7.304e+009	-7.304e+009
Liq vol flow at std cond (m ³ /h)	997.2*	997.2
	Properties	
	Overall	Liquid Phase
Molecular weight	44.03	44.03
Molar density (kgmole/m ³)	19.51	19.51
Mass density (kg/m ³)	859.2	859.2
Act. volume flow (m ³ /h)	947.6	947.6
Mass enthalpy (kJ/kg)	-8970	-8970
Mass entropy (kJ/kg-C)	2.344	2.344
Heat capacity (kJ/kgmole-C)	108.1	108.1
Mass heat capacity (kJ/kg-C)	2.456	2.456
Lower heating value (kJ/kgmole)	902.5	902.5
Mass lower heating value (kJ/kg)	20.50	20.50
Phase fraction (vol. basis)	-	1.000
Phase fraction (mass basis)	2.122e-314	1.000
Partial pressure of CO ₂ (kPa)	0.0000	-

* Material stream: CO₂; Fluid package: Basis-1; Property package: Peng-Robinson

geothermal gradient of 30°C/km. For the subsurface study, we applied a linearly increasing salinity gradient of 1 (mol/L)/km of NaCl from zero salinity at the surface. This reflects the background tendency for salinity to increase with depth, but in real formations we might expect more-discrete changes across different units.

Option 1: Standard Injection Strategy

The standard method involves injection of compressed CO₂ in a dense supercritical phase into a saline aquifer for geologic storage. Bachu (2002) suggests that to reduce costs associated with injection and to limit the buoyancy forces and maximize the mass of free CO₂ that can fill a given pore volume, CO₂ should be injected in a supercritical state. However, CO₂ injected in supercritical state has a much lower density and viscosity than the liquid brine it displaces at conditions in the geologic formation. The injection of CO₂ occurs under deep depths, greater than 800 m, to ensure that the CO₂ is in the dense phase.

The HYSYS model of the standard injection facilities was developed and used to investigate the important design and operation variables. A description of the conceptual standard bulk-phase injection strategy with process flow diagram (PFD) is found in Fig. 5. The standard approach could be conducted by injection of CO₂ into an aquifer. Dense-phase CO₂ has a density of approximately 700 kg/m³, leaving a density difference between the CO₂ and formation fluids of approximately 300 kg/m³ (Fig. 4b), which drives the buoyant migration of CO₂ toward the top of a reservoir layer. This technique relies on the presence of a caprock with a capillary entry pressure sufficient to hold the CO₂.

Option 2: CO₂/Brine Surface-Mixing Strategy

The CO₂/brine surface mixing and injection method is an important and perhaps an essential step for the secure storage of CO₂ because it removes buoyant vertical migration in the reservoir. For example, once the CO₂ is dissolved in brine, it will no longer migrate upward as a separate phase. Once dissolved, it will travel at the same rate as the native formation fluids, which may remain underground for millions of years before discharging at the surface.

The CO₂/brine mixing study was performed in the surface pressure mixing vessel. A surface-dissolution approach involves dissolving captured dense CO₂ into brine in surface facilities, and the CO₂-saturated brine is then injected into the storage formation. The brine required for the surface mixing is extracted from same formation used for storage.

We modeled the mixing vessel in HYSYS with a tank. The most important design variables in the mixing vessel are power consumption and residence time required to accomplish the mixing process. The rate at which CO₂ dissolves into the brine is a key constraint on the duration of possible complete dissolution. Considering the previous findings (Hangx 2005), which suggest 90% dissolution of static CO₂ into brine in 9 minutes at a pressure range from 330 to 580 psia. Retention times less than 9 minutes would be required at the elevated pressures, but specific design criteria require further work. The mixing vessel has been designed to provide maximum flexibility over a wide range of operating conditions. The dense-phase CO₂ stream enters the vessel at a temperature of 30.20°C and a pressure of 1,088 psia (7499 kPa or 74.99 bar). The brine stream also enters with similar pressure but lower temperature [22.39°C and 1,092 psia (7526 kPa)]. This

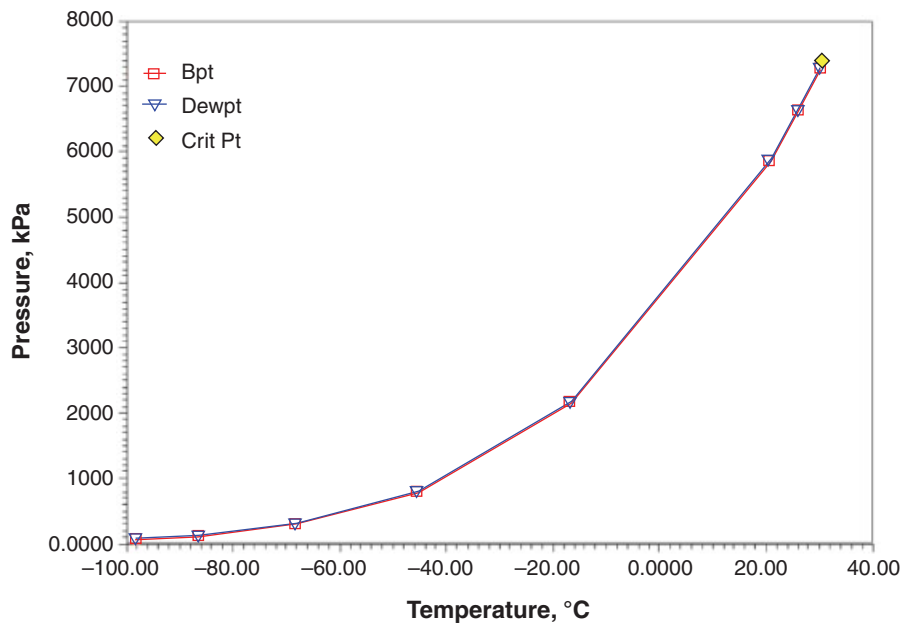


Fig. 1—Pure-CO₂ P/T phase envelope.

method proves to be efficient because the simulation results show that greater pressure and lower temperatures increase solubility in the mixing vessel. Because of the phase behavior of the CO₂ stream, the mixing operation requires minimum pressure of 7 433 kPa (1,078 psia), which is the critical pressure of CO₂. The facilities design and simulation results of this study show that pressure below CO₂ critical pressure is problematic and thus should be avoided. The process facilities and the mixing vessel are optimized around the operating condition in an attempt to predict the chemical interaction between supercritical CO₂ and the brine.

The basic process-optimization challenge is the operating temperature and pressure of the mixing vessel, which have a strong link with the brine/CO₂ solubility. Lower temperature in the brine stream was optimized against high pressure to maximize CO₂/brine dissolution in the mixing vessel. Furthermore, the phase behavior of the

mixing-vessel product (CO₂-saturated brine steam) (Fig. 6) is quite strange, and care should be taken in the design of the facilities and operation of the stream. The stream behavior is relatively different from a supercritical-CO₂ stream and is closer to the brine stream. This great influence of the product stream toward the brine stream is closely linked with the high boiling point of brine (Fig. 6). The flow rate of the CO₂ stream used in the design is 1311 kg mol/h [on the basis of 5 × 10⁵ tonnes (11 484 360 kg mol) of CO₂ per year], and the flow rate of brine is 2515 kg mol/h (Fig. 7). Because of the low solubility of the CO₂ in the brine, a large volume of brine is necessary to dissolve a given amount of CO₂. A further concern is the degassing of CO₂ from the solution as the hydrostatic pressure descends below the critical pressure. Degassing can occur if pressure drops beneath the critical pressure, and hydrates can form if temperatures drop certain parameter below critical condition.

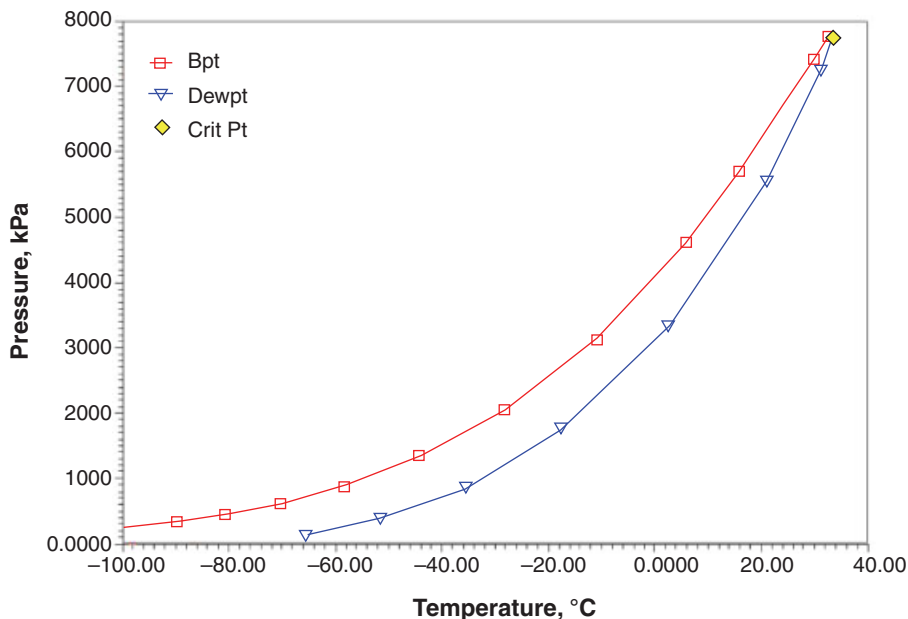


Fig. 2—CO₂ with 5% impurities P/T phase envelope.

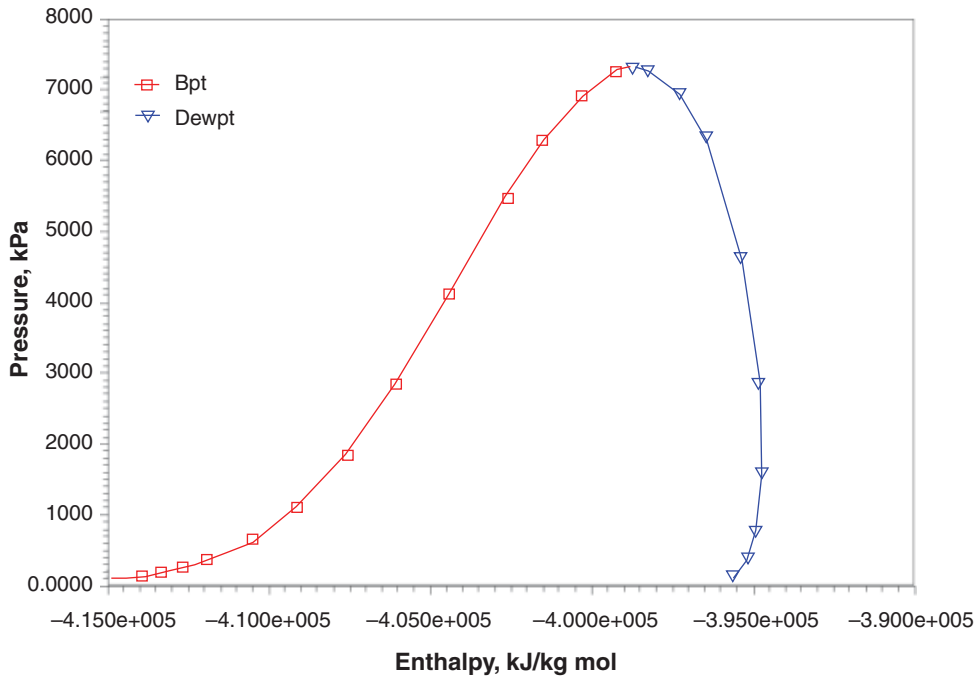


Fig. 3—CO₂ P/H phase envelope.

Gravity-driven flow induced by the increased density of CO₂-saturated brine is necessary to contact this large volume of brine and, therefore, determines the long-term dissolution rate. Depending on the brine salinity, the flow rate of brine required for the dissolution of CO₂ could be two to 10 times higher than the flow rate of

CO₂. However, a lower brine flow rate is possible with a higher-pressure vessel. The operating condition of the mixing vessel can be optimized to save cost and hence could be different from that of other surface process facilities. Considering the proposed CO₂-brine-flow rates and residence time proposed in the preceding, the

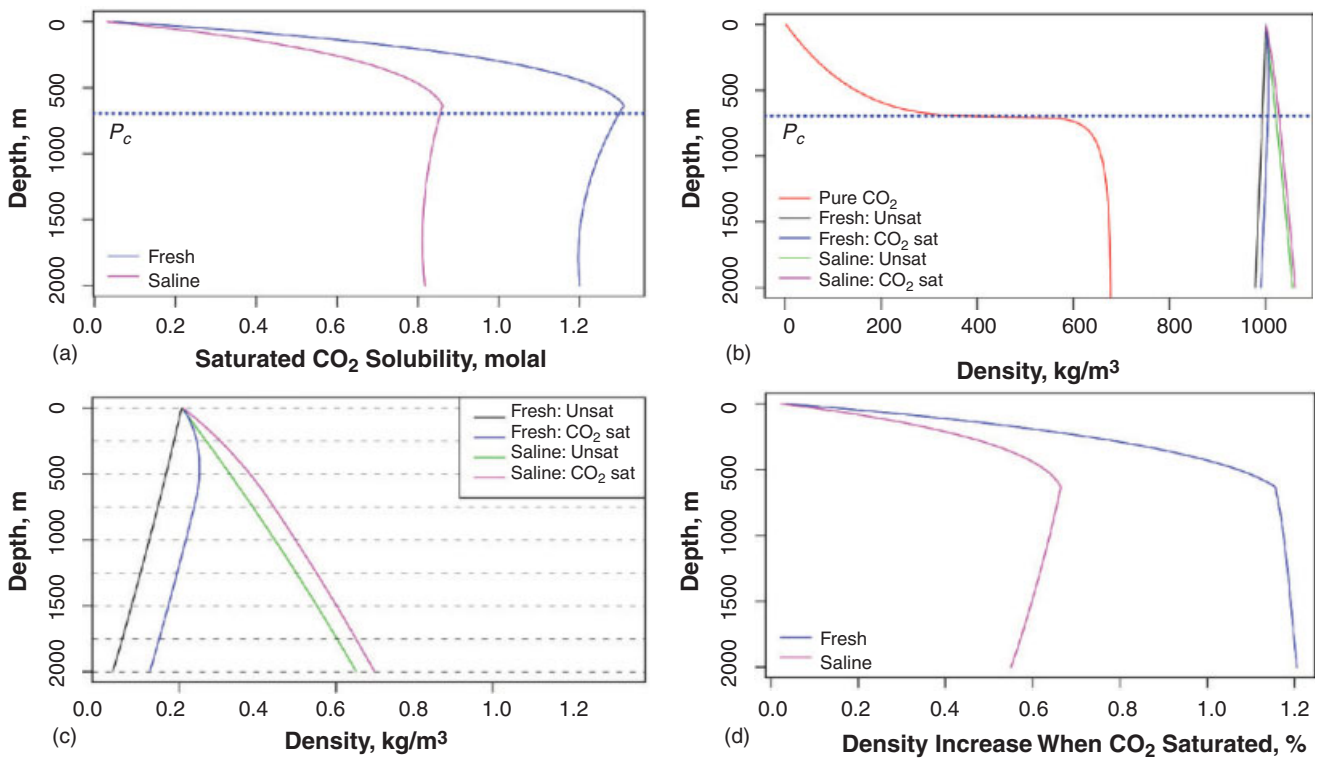


Fig. 4—Downhole properties of pure CO₂, pure fresh water, brine, CO₂-saturated fresh water, and CO₂-saturated brine. (a) Solubility of CO₂ in fresh water and brine, (b) density of pure CO₂ and fluids, (c) zoom in on the fluid densities, and (d) percentage increase in fluid density as a consequence of saturating the pure fluid with CO₂. Salinity increases with depth at (1 mol/L)/km.

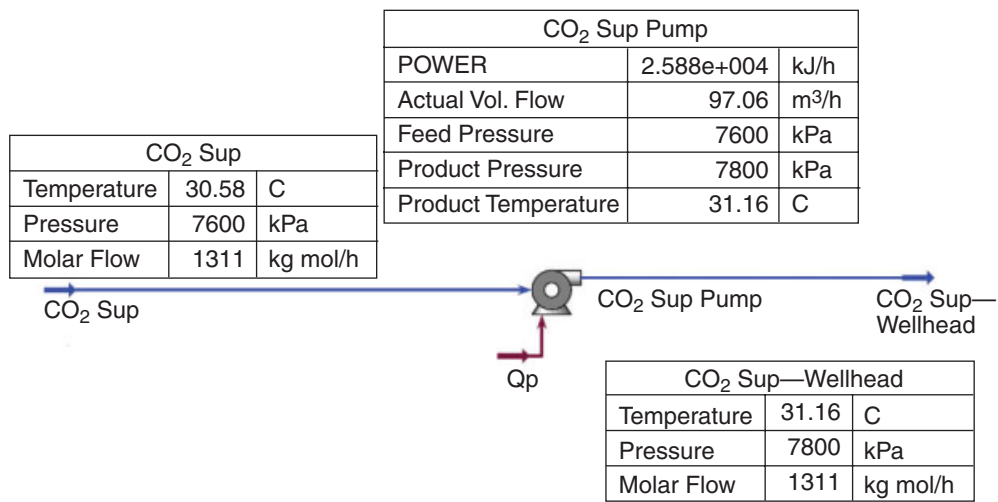


Fig. 5—Standard-injection-process simulation PFD.

size of the cylindrical mixing vessel required to handle such volume is approximately 4.0 m in diameter and 12.3 m in height [estimated with cylinder-volume equation (Engineers Edge 2000)],

$$V = 0.7854d^2h \dots \dots \dots (8)$$

Considering the large size of this pressure vessel, multiple vessels with smaller diameter are suggested as having a more-viable process capability. The pressure mixing vessel is the most important operation unit in this flow scheme because material streams (CO₂, brine) are combined. A detailed process pressure vessel is normally designed in accordance with the ASME boiler and pressure vessel code and is beyond the scope of this paper. Therefore, the simulation is constructed simply as a mixing tank with the operating conditions specified. This design is a first theoretical stage of analyzing the surface mixing vessel; much more detailed work on the physical equipment and the costing still needs to be undertaken. A description of the conceptual CO₂/brine surface mixing and injection strategies with a PFD showing pipeline segments is found in Fig. 6.

In order to operate the mixing strategy in the pressure mixing vessel, the brine and the CO₂ are brought up to a similar pressure

for mixing with pump and control valve, respectively; so the power requirement is the sum of the brine and CO₂ power curves. The brine pump boosts the brine pressure to the required operating pressure of the mixing vessel, which must be equal to or greater than the critical pressure of the CO₂ stream. The control valve is designed to force process fluids through a series of control stages of pressure letdown. The control valve removes kinetic energy from the fluid and lowers pressure in a controlled manner to suit the pressure required in the mixing vessel. The full steady-state mixing-vessel pressure or instrument control varies and is not covered in this study. The mixing pressure should normally be in the range needed for injection but could be a step up or down as required to equal the wellhead pressure, and the range is dependant on the storage-formation condition.

The simulation provides functions that allow stream rate, velocity in the pipeline, a vessel temperature or pressure, or other factor to be varied in order to meet some desired output rate (e.g., complete CO₂/brine dissolution). Similarly, the process facilities are controlled to meet product specifications such as supercritical CO₂ or single-phase-flow regime. The properties of the streams in the pipeline and other facilities (Fig. 8) (Tables 2 and 3) show the behavior of the streams and flow performance. The size of pipeline

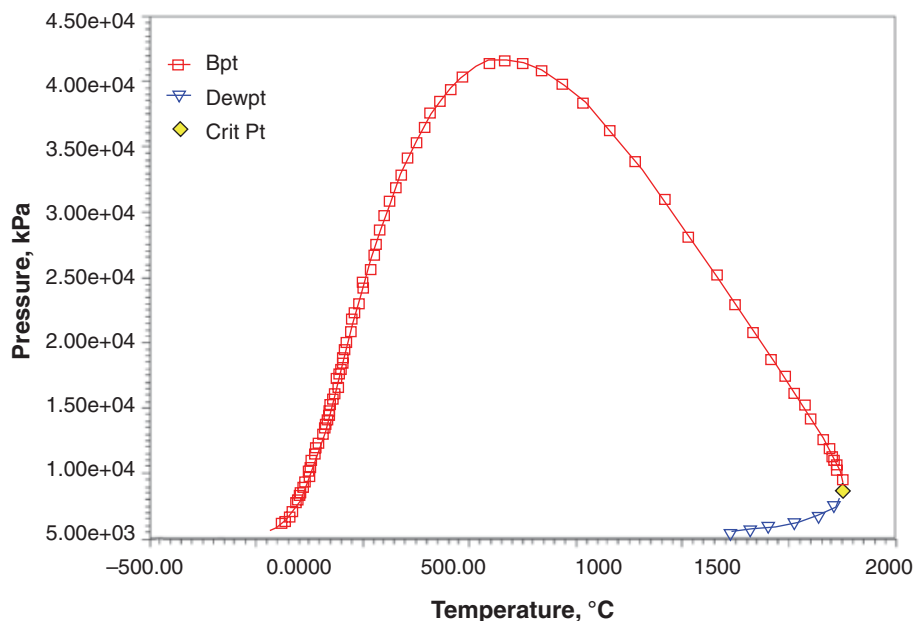


Fig. 6—CO₂-saturated brine-stream phase envelope.

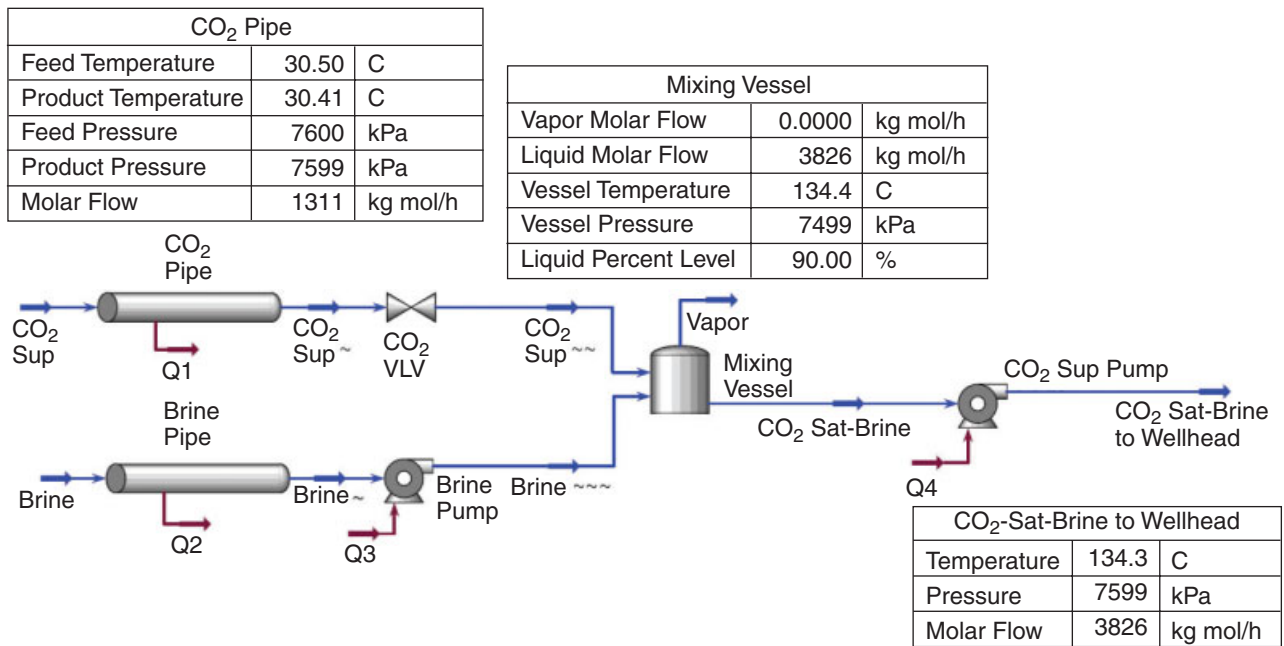


Fig. 7—CO₂/brine surface-mixing process simulation PFD.

depends on the amount of materials handled, and the distance of 600 m from the surface injection facilities (onshore storage site) to the wellhead is proposed because the injection facilities should be close to the injection wellhead (Table 2); however, this could be more distant in the case of an offshore storage site. As can be seen in Table 3, the flow regime in the entire pipe segment remains liquid only, indicating that the stream is in single phase. The conditions that the streams experience in the mixing vessel are very important because the dissolution of CO₂ in brine and hydrate formation depend on them.

Complete dissolution of CO₂ in brine is considered as a significant impact on strategy because it would influence engineering considerations for design and operation of CO₂-injection wells. The feasibility of a strategy in which dense CO₂ is dissolved in brine at the surface facilities is investigated by comparing the CO₂-saturated brine density to density of native brine without CO₂. The

CO₂-saturated brine is slightly denser than native brine without CO₂ (Figs. 4c and d) and, hence, has a downward buoyancy drive. This is a significant advantage because it removes the need for a perfect seal and the fluid can be injected safely at shallower depths than the pure CO₂. Further, the production of brine from deeper intervals within the reservoir would induce a pressure drawdown that enhances the migration of the CO₂-saturated brine away from the injection site while providing a mechanism to regulate the reservoir pressure. This appears to be a promising option, but needs further evaluation for energy and equipment costs.

Option 3: CO₂/Water Surface Mixing

Dissolving CO₂ in water forms carbonic acid (carbonated water), this makes CO₂ much less buoyant in the subsurface. Dissolved CO₂ when stored in a geological formation may assist transformation into carbonate minerals (Eqs. 2 through 7) (Gunter

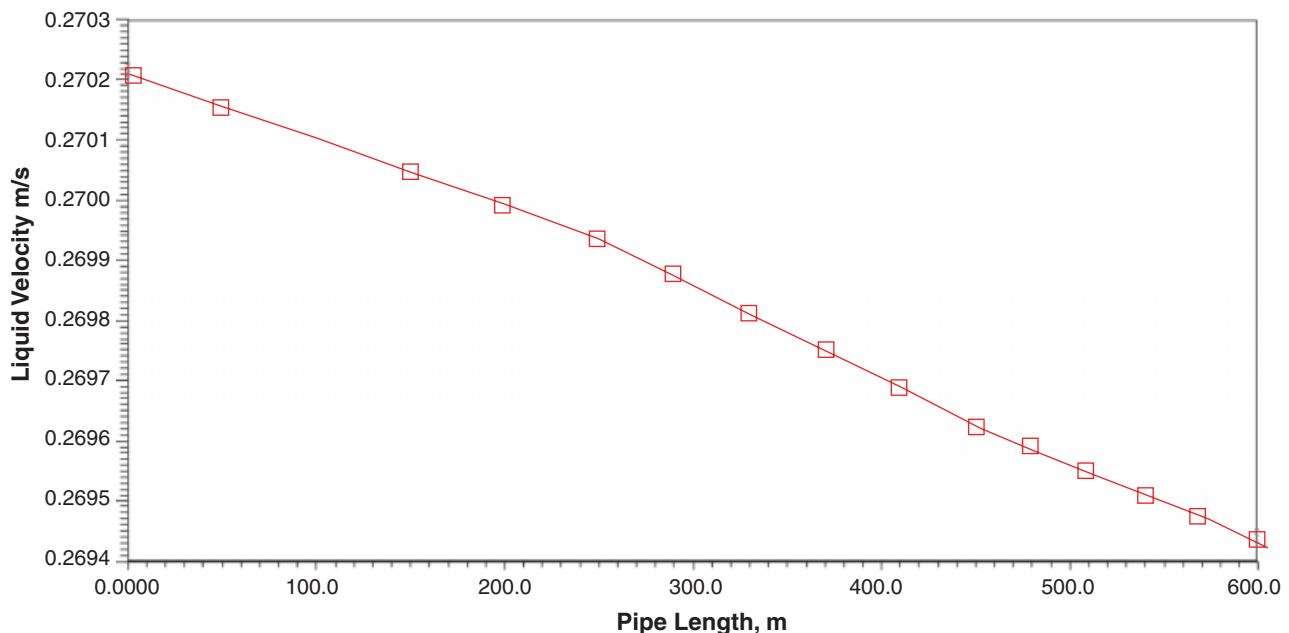


Fig. 8—Liquid velocity across the pipeline.

TABLE 2—PIPELINE SIZING PARAMETERS			
Pressure Gradient/Pipe Parameters			
Pipe Flow Correlation	Pressure Drop		
Beggs and Brill	0.5896 kPa		
Sizing			
Segment Number	1	2	3
Fitting/pipe	Pipe	Pipe	Pipe
Distance (m)	250.0*	200.0*	150.0*
Elevation change (m)	6.000*	-6.500*	0.5000*
Schedule	Schedule 40	Schedule 40	Schedule 40
Nominal diameter (mm)	355.6	355.6	355.6
Outer diameter (mm)	355.6	355.6	355.6
Inner diameter (mm)	333.3	333.3	333.3
Material	Mild steel	Mild steel	Mild steel
Roughness (m)	4.572e-005	4.572e-005	4.572e-005
Conductivity (W/m-K)	45.00	45.00	45.00
Increments	5	5	5

et al. 2004). This injection strategy investigates the possibility of enhancing the process by performing the mixing in the surface facilities. Predicting the sequestration potential and long-term behavior of geologic formations requires calculating the pressure, temperature, and composition properties of CO₂/H₂O mixtures at depths where temperatures remain below 100°C, but where pressures vary and may reach several hundred bar. Dense CO₂ is mixed with water in surface facilities before injection into the geological formation (Fig. 9). A mixing vessel was used in Fig. 7 (CO₂/brine dissolution) because of low solubility of the CO₂ in the brine (Fig. 3a), which requires more-rigorous pressure-vessel operation to achieve dissolution; but the solubility of CO₂ in fresh water is higher, and dissolution could be achieved easily with pipe mixing. Recent further studies on mixing and reaction technology suggest that an in-line mixer is the optimal process facility capable of bringing enduring solutions to this operation. Hence, success in application of this concept, especially to offshore injection sites, depends on adopting in-line-mixer technology. Furthermore, high-pressure mixing vessels are not the answer for all mixing tasks because this capability can often be provided by in-line mixers or blenders. The carbonated water requires special handling to avoid hydrate formation in the pipeline and special materials of construction that must be resistant to the corrosive action of the carbonated stream.

When CO₂ dissolves in water, it forms a carbonic liquid that is less dense than the expected ambient saline formation fluid (by approximately 50 kg/m³ for the parameterizations chosen here and at reservoir depths; see Fig. 4c); hence, an upward potential flow is expected. However, this density difference is an order of magnitude lower compared with that of supercritical CO₂. The use of seawater rather than pure water would help to reduce this buoyancy drive, at the expense of lower CO₂ solubility. A major limitation with this strategy is that it requires the injection of significant volumes of water (at least an order of magnitude greater than what is required for the standard injection of pure CO₂) into the formation. Because the saturated fresh water is buoyant, it requires the presence of a seal to retain it; the performance of a capillary seal in a water-wet reservoir-seal system is likely to be low. A further concern is the degassing of CO₂ from the solution as the hydrostatic pressure drops beneath the critical pressure. Degassing can occur if pressure drops beneath the critical pressure, and hydrates can form if temperatures drop below critical condition. In summary, this does not appear to be a good option. The simulation results show that free water is found in the carbonated-water stream and that hydrate is formed at the moderate temperature of 10°C. These

conditions make handling of a carbonated-water stream in the process facilities very problematic. Moreover, dehydration of the carbonated-water stream is not possible at the given operation condition, and handling of wet CO₂ with free water implies high corrosion potential. Hence, the stream is not transportable in carbon-steel pipes; however, inhibitor could be added in carbon-steel pipes to reduce the impact of corrosion, as suggested by Cosham and Eiber (2007) and previously discussed in the section that addresses materials considerations. We recommend that corrosion-preventive actions be evaluated and implemented, which includes choosing correct operating conditions and corrosion-resistant materials. The construction material recommended for use in this type of process is 304/316L stainless steel, which has been proved to provide the best corrosion resistance.

Option 4: CAB Injection Strategy

Operation strategy that alternates supercritical CO₂ with brine injection was simulated. In this method, the supercritical CO₂ and brine are injected alternately (Fig. 10). This strategy is based on the water-alternating-gas model. The model involves two standard injection facilities with one pumping the CO₂ stream and the other pumping the brine stream to the wellhead where the alternating-injection schedule is operated. This injection strategy is expected to reduce CO₂-buoyancy migration and immobilize CO₂ in the formation. Research is under way elsewhere in the CO₂ Aquifer Storage Evaluation Site and Monitoring (CASSEM) project to explore the effects of this strategy in CO₂/brine pore-scale mobility and investigate predictions of the changes to capillary forces, residual saturation, and density of injected fluids (CAB) relative to reservoir fluids.

Conclusions and Recommendations

The conceptual injection strategies, designs, and simulations proposed in this paper address long-term CO₂-storage uncertainties and concerns. The study could serve as the basis for determining whether further work should be conducted on the proposed process. The interaction of a supercritical-CO₂ stream with other streams (brine and water) and their behavior in the process facilities were predicted in various operating conditions relevant to geological formations. Our study of the injection of a CO₂-saturated-brine stream demonstrates that surface dissolution facilities enhance CO₂/brine solubility and directly improve CO₂ sequestration.

The findings show that dissolving CO₂ into brine at the surface facilities before injection into geologic formations produces a CO₂-saturated-brine stream with density slightly higher than the

TABLE 3—PIPELINE-SEGMENT PROFILE AND OPERATING CONDITIONS				
Heat Transfer				
<u>Heat Loss</u>	<u>Ambient Temperature</u>		<u>Overall HTC</u>	
2.859e+004 kJ/h	0.5000°C		1.425 kJ/h·m ² ·C	
Inside Heat Transfer Coefficient Estimation				
<u>Include Inner HTC</u>		<u>Correlation</u>		
Enabled		Profes		
Pipe Wall Resistance Estimation				
<u>Include Pipe Wall Resistance</u>				
Enabled				
Insulation Resistance Estimation				
<u>Include Conduction</u>	<u>Type</u>	<u>Thermal Conduction</u>	<u>Thickness</u>	
Disabled	Urethane foam	1.800e-002 W/m·K	1.000e-002 m	
Outside Heat Transfer Coefficient Estimation				
<u>Include Outer HTC</u>	<u>Ambient Medium</u>	<u>Ground Type</u>	<u>Ground Conductivity</u>	<u>Buried Depth</u>
Enabled	Ground	Dry peat	0.1700 W/m·K	1.000 m
Profiles				
<u>Data</u>				
<u>Distance (m)</u>	<u>Elevation (m)</u>		<u>Increments</u>	
0.0000	0.0000		5	
250.0	6.000		5	
450.0	-0.5000		5	
600.0	0.0000		-	
Pipe Table				
Length (m)	0.0000	50.00	100.0	150.0
Elevation (m)	0.0000	1.200	2.400	3.500
Pressure (kPa)	7600	7592	7584	7576
Temperature (°C)	30.50	30.47	30.45	30.42
Vapor fraction	-	-	-	-
Heat transferred (kJ/h·m)	-	47.73	47.69	47.65
Flow regime	Liquid only	Liquid only	Liquid only	Liquid only
Liquid holdup	1.000	1.000	1.000	1.000
Friction gradient (kPa/m)	1.052e-003	1.052e-003	1.051e-003	1.051e-003
Static gradient (kPa/m)	0.1611	0.1611	0.1612	0.1612
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000
Liq. Reynolds	9.931e+005	9.923e+005	9.916e+005	9.906e+005
Vap. Reynolds	-	-	-	-
Liquid velocity (m/s)	0.2702	0.2702	0.2701	0.2701
Vapor velocity (m/s)	-	-	-	-
Deposit thickness (mm)	-	-	-	-
Depository volume (m ³)	-	-	-	-
Length (m)	200.0	250.0	290.0	330.0
Elevation (m)	4.800	6.000	4.700	3.400

original brine in the formation. The denser CO₂-saturated-brine stream when injected into the formation is capable of eliminating the buoyancy force that is a strong driving force to bring CO₂ to the surface. Moreover, CO₂/brine surface dissolution proves to be the primary strategy to speed up CO₂ immobilization because the period of time needed to achieve immobilization in the subsurface formation is reduced by the surface mixing vessel. Immobilized CO₂ will remain in place indefinitely even if the integrity of the seal is not intact. No additional time is required for immobiliza-

tion after injection ends. Thus, CO₂/brine surface-mixing strategy is recommended because it is directly linked with enhanced and secure storage of CO₂ in geologic formations. It is clear that CO₂/brine surface mixing and injection form the best of the four injection strategies considered in this study. Mobile dense-phase CO₂ is dependent on the integrity of the geological-formation seal and requires monitoring. CO₂/water surface dissolution is comparable to CO₂/brine surface dissolution technically, despite pitfalls associated with the carbonated-water-stream handling.

TABLE 3—PIPELINE-SEGMENT PROFILE AND OPERATING CONDITIONS (Continued)				
Pressure (kPa)	7568	7559	7568	7577
Temperature (°C)	30.39	30.37	30.38	30.40
Vapor fraction	—	—	—	—
Heat transferred (kJ/h-m)	47.61	47.56	47.59	47.61
Flow regime	Liquid only	Liquid only	Liquid only	Liquid only
Liquid holdup	1.000	1.000	1.000	1.000
Friction gradient (kPa/m)	1.051e-003	1.051e-003	1.051e-003	1.050e-003
Static gradient (kPa/m)	0.1612	0.1613	-0.2184	-0.2185
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000
Liq. Reynolds	9.901e+005	9.894e+005	9.895e+005	9.897e+005
Vap. Reynolds	—	—	—	—
Liquid velocity (m/s)	0.2700	0.2699	0.2699	0.2598
Vapor velocity (m/s)	—	—	—	—
Deposit thickness (mm)	—	—	—	—
Deposit volume (m ³)	—	—	—	—
Length (m)	370.0	410.0	450.0	480.0
Elevation (m)	2.100	0.8000	-0.5000	-0.4000
Pressure (kPa)	7586	7594	7603	7602
Temperature (°C)	30.41	30.43	30.44	30.44
Vapor fraction	—	—	—	—
Heat transferred (kJ/h-m)	47.63	47.66	47.68	47.67
Flow regime	Liquid only	Liquid only	Liquid only	Liquid only
Liquid holdup	1.000	1.000	1.000	1.000
Friction gradient (kPa/m)	1.050e-003	1.050e-003	1.050e-003	1.050e-003
Static gradient (kPa/m)	-0.2185	-0.2186	-0.2186	2.243e-002
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000
Liq. Reynolds	9.898e+005	9.900e+005	9.901e+005	9.899e+005
Vap. Reynolds	—	—	—	—
Liquid velocity (m/s)	0.2698	0.2697	0.2696	0.2696
Vapor velocity (m/s)	—	—	—	—
Deposit thickness (mm)	—	—	—	—
Deposit volume (m ³)	—	—	—	—
Length (m)	510.0	540.0	570.0	600.0
Elevation (m)	-0.3000	-0.2000	-1.000e-001	0.0000
Pressure (kPa)	7602	7601	7600	7599
Temperature (°C)	30.43	30.42	30.42	30.41
Vapor fraction	—	—	—	—
Heat transferred (kJ/h-m)	47.66	47.65	47.64	47.63
Flow regime	Liquid only	Liquid only	Liquid only	Liquid only
Liquid holdup	1.000	1.000	1.000	1.000
Friction gradient (kPa/m)	1.049e-003	1.049e-003	1.049e-003	1.049e-003
Static gradient (kPa/m)	2.243e-002	2.243e-002	2.244e-002	2.244e-002
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000
Liq. Reynolds	9.897e+005	9.894e+005	9.892e+005	9.890e+005
Vap. Reynolds	—	—	—	—
Liquid velocity (m/s)	0.2696	0.2695	0.2695	0.2694
Vapor velocity (m/s)	—	—	—	—
Deposit thickness (mm)	—	—	—	—
Deposit volume (m ³)	—	—	—	—

There is a need for further research to address gaps in our knowledge about large-scale CO₂ interaction with and behavior in the surface facilities and subsurface formations. Further studies are under way to address injection/extraction, pipeline, surface equipment, and energy costs of each option proposed. More research is required to advance the operations of problematic streams in the process facilities and to understand the impact of impurities on the equipment.

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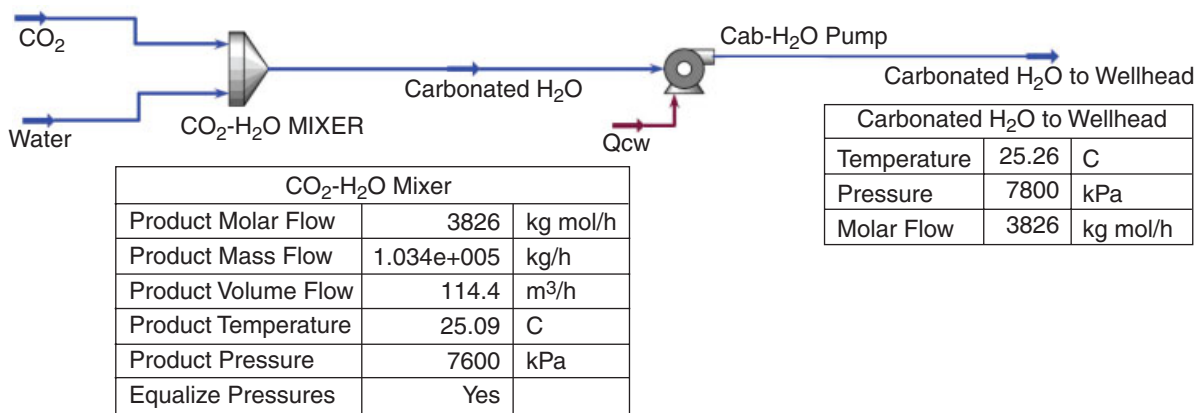


Fig. 9—CO₂/water surface-mixing-process simulation PFD.

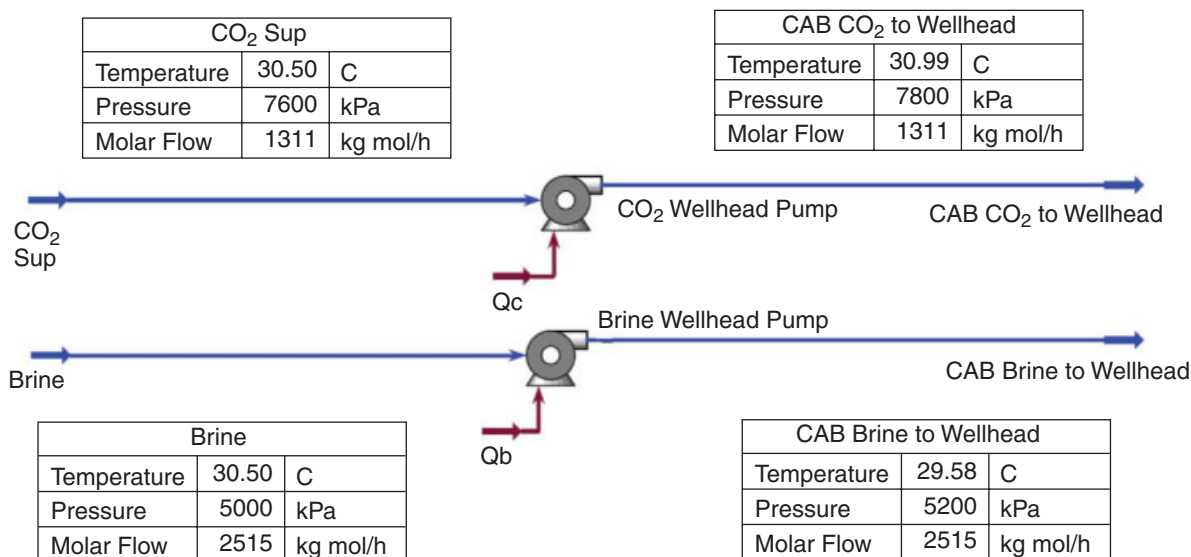


Fig. 10—CAB-process simulation PFD.

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