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CO₂-Brine Surface Dissolution and Injection: CO₂ Storage Enhancement

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Abstract

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 which has carefully evaluated details of performance during and after the injection process. Standard methods of site evaluation for saline aquifers focus overwhelmingly 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 (1-50yr) and storage distributions in the long term (1,000 – 10,000 yr). 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. Human society seems to have an insatiable appetite for fossil fuels and now consumes about 13 Terrawatts (1 TW = 10¹², W = 3.2 EJ/year) of energy worldwide, and approximately 80% of that comes from burning fossil fuels [1]. Kaya [2] 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, carbon-based fuels used for energy production, C, and modified by Hoffert et al [3] to include CO₂ sinks, S_{CO₂}, hence C is expressed:

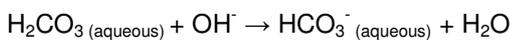
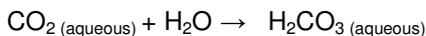
$$C = P \frac{GDP}{P} \frac{E}{GDP} \frac{C}{E} - S_{CO_2} \quad (1)$$

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 (C/E). The term E/GDP reflects the sectorial make-up 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 [4]. 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 like China and India, with no absolute reduction in established emitters such as the USA or the EU.

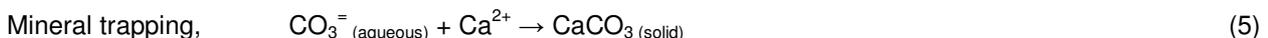
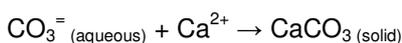
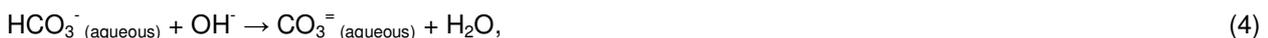
CCS is widely recognized as an important option to reduce atmospheric carbon dioxide emissions. Specifically, CCS has the potential to provide emissions cuts sufficient to stabilize greenhouse gas levels, while still allowing for the continued use of fossil fuels [5]. This can act as a transitional technology, 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 [6], 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 oil production into oil and gas fields. It is estimated that saline aquifers have the largest volume potential to store CO₂ worldwide. The IEA Greenhouse Gas Research and Development Programme [7] estimated in the early 1990s that the global potential for storage of CO₂ in deep saline reservoirs is between 400 and 10,000 Gtonne CO₂. Deep saline aquifers have the largest storage capacities, amongst the geological storage options. Deep saline aquifers are present in most countries, storage locations are not limited to hydrocarbon-bearing areas. Many saline formations are not extensively explored, characterised or assessed for CO₂ storage. Geologic information about specific sites is more limited than for oil and gas fields, and 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 towards potable water areas. If CO₂ leakage to the surface occurs, there is a potential for upwards mobilisation of heavy metals from deeper saline brine and contamination of drinking water. To reduce uncertainties, evaluation of saline formations using reservoir modelling simulations is a useful first step, potentially followed by test drilling and injection. An enhanced ability to monitor and verify the behaviour of geologically stored CO₂ may also be needed.

Geological CO₂ storage for long timescales (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 via 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 trappings - the process of forming in situ, interstitial carbonate minerals from CO₂ and the host rock and formation waters [8]. Most of the trapping mechanisms are interconnected. The most basic chemical reactions that lead to solubility trapping and mineral carbonation are [9]:



Ionic trapping



Although more complex reactions may also take place with Ca and Mg rich minerals [9, 10], subsurface mineralization is a slow long-term process which is strongly dependent on the availability of reactive minerals, such as Ca-rich feldspars, Mg/Fe-rich clays and micas, Fe-oxides or olivine [11].

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 which are generally well understood [12, 13]. CCS appears to be achievable from a technical perspective, although there are significant issues of scale-up and optimisation 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 both about its buoyancy and migration underground, as well as the possibility of leakage and escape to the surface [13]. Surface releases would undermine efforts to stabilize atmospheric CO₂ concentrations, and could, in a worst case scenario, pose environmental and human health risks [13]. 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 the geological formation. Risk in its engineering definition is the product of the likelihood of an event to occur and the consequences of the event-taking place [4]. The risks associated with CO₂ surface and injection facilities are well understood and documented [14].

Successful storage of CO₂ in the geological formations such as Utsira aquifer (for Sleipner field) [15] and enhanced oil recovery at Weyburn [16] relies on an impermeable seal at the top of the formation to trap the fluid CO₂ [17]. 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, assuring perfect containment is more difficult in less-known aquifer formations with possible faulty seal or wells [18, 4] 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 on-going 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 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 behaviour of CO₂ since it can cause considerable process concerns, particularly with respect to possible phase changes. Carbon dioxide at critical temperature and pressure (i.e. $T_c = 30.978\text{ }^\circ\text{C}$, $P_c = 7.3773\text{ MPa}$) has a density of about 467.6 kg/m^3 [19] 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 800m 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 [8]. 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, softwares 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 which may be able to gain acceptance. Here, we study innovative concepts that could tackle these uncertainties and enhance the 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 here 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 behaviour of CO₂ in process facilities. The important predictions required were density of injected CO₂ relative to brine, 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 strategies 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 equipments, and to perform a comprehensive sensitivity analysis at any point. This research project use 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 softwares used for the modelling 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 non-linear) solved using relatively sophisticated techniques. The softwares 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 analyse the behaviour 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, vapour liquid equilibria, calculated physical properties, equipment performance, etc. 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 [20], pure water and brine [21]; solubilities of CO₂ in pure water and brine [22 and 23] and CO₂ saturated fluid densities [24].

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 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, pumps, the injection wellhead, downhole and monitoring equipment. This paper will address components 1 and 2 peripherally but focus on 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. 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 minimise 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 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 billion cubic feet per day of dry CO₂ is compressed to between 900 to 2,000 psi and transported 500 miles [25]. Adapting this knowledge, power stations will dry CO₂ streams to the level required to prevent hydrate formation / internal corrosion, 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, viton, etc are considered to be appropriate for use in valves, control seals and packing. ASME code should be used to specify maximum design pressures of pipe or flanges. 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 involves handling of 'wet' CO₂ (e.g. containing free water) with high corrosion potential and therefore not transportable in carbon steel pipes. Cosham [26] suggests 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 equipments should be constructed with stainless steel. This is a high performance option, but costly.

The injection pump is designed to increase the pressure of the CO₂ to the required injection conditions. Pipeline around injection facilities is selected based on 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 due to shift in temperature during injection. The CO₂ pump and wellhead pressure is expected to be a function of CO₂ injection rate at initial reservoir pressure and at formation fracture pressure.

Model construction

The injection strategies 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), etc.), process flow diagram (pieces of equipment are connected together), process equipment data (pipeline profile, pump/compressor performance curves or efficiency, etc). The models were constructed with the least equipment possible whilst adequately modelling the process.

Generally, the simulations were used to determine how the streams entering the process behave (stream enthalpies, equipment performances, etc) and ensuring the flow regime of products exiting the process in this case remains in single phase (liquid only/dense phase). Considering generic case for the injection strategies models, the stream conditions and properties used (table 1) is same. HYSYS performs rigorous mass and energy balances of each injection process based on the equation of state (Peng-Robinson [27]) selected. Descriptions of the constructed injection strategies models are presented.

Table 1 CO₂ Stream Conditions and Properties

Material Stream: CO₂		
Fluid Package:		Basis-1
Property Package:		Peng-Robinson
CONDITIONS		
	Overall	Liquid Phase
Vapour / 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 @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	---

Phase behaviour

The first step in calculating any injection scenarios is the calculation of the phase envelope. A good understanding of fluid phase behaviour is very important in the design of 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 behaviour and physical properties were important in all aspects of the injection methods. The simulations employ an equation of state package that treats multi-component 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 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-Robinson [27] equation of state which provides an accurate reflection of the behaviour of streams.

We calculated and constantly monitored the CO₂ stream properties in the facilities such as temperature, pressure (Figs. 1a and 1b), enthalpy (Fig. 2) 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 (about 5%) in the captured CO₂ stream has huge negative impact in the phase behaviour of the stream and imposes major operational problem in the process facilities. As shown in Fig. 1a with pure CO₂ stream and Fig.1b for CO₂ stream with 5% impurities, operating at conditions below critical point is problematic and should be avoided.

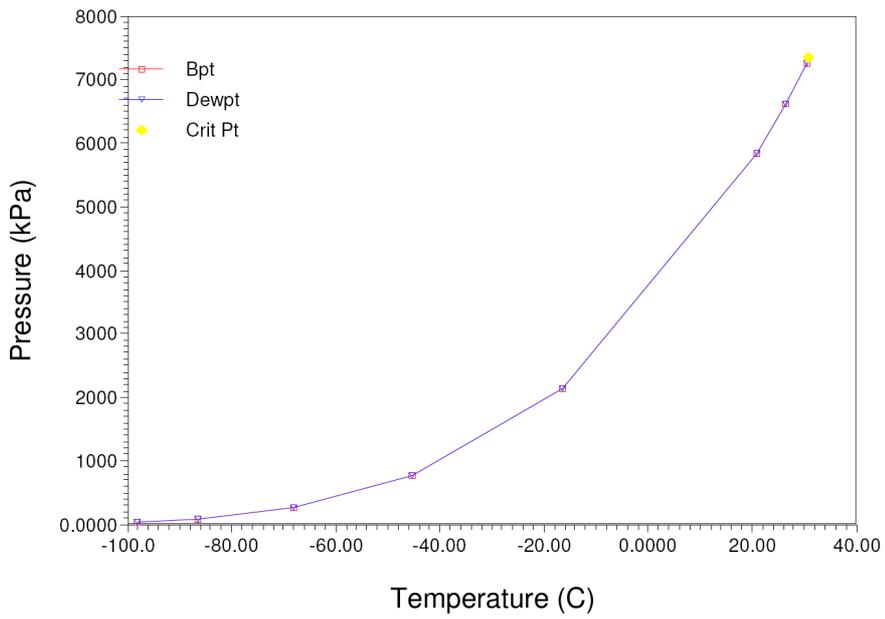


Fig. 1a. Pure CO₂ P-T phase envelope

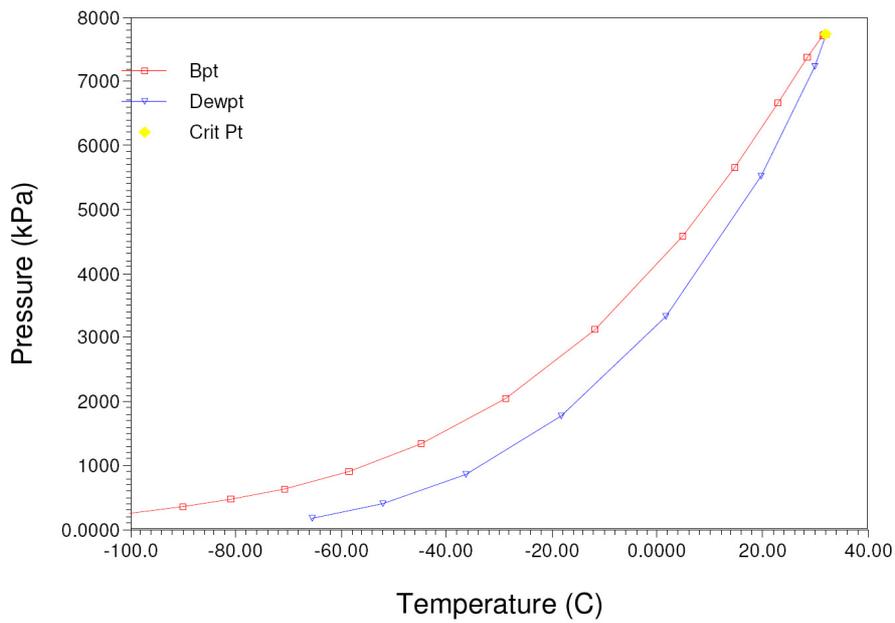


Fig. 1b. CO₂ with 5% impurities P-T phase envelope

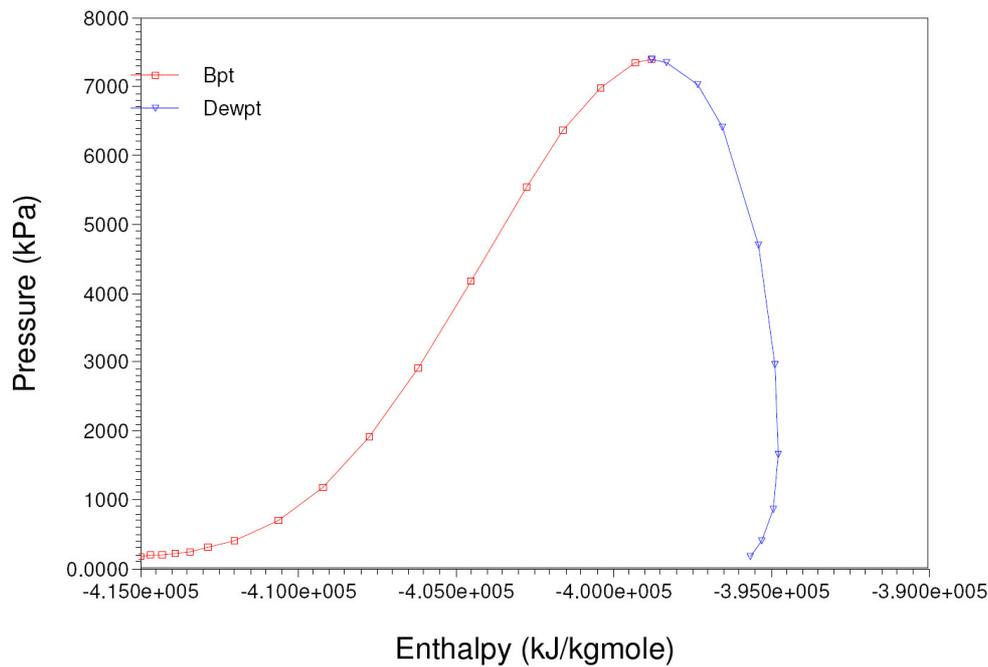


Fig. 2. CO₂ P-H phase envelope

Subsurface properties

We have investigated the subsurface phase, solubility and densities of materials relevant to this study (Fig. 3). 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 Huang [20]. The density of the pure water and brine were calculated following Danesh [21]. The solubilities of CO₂ in pure water and brine were calculated using Spycher [22 and 23]. The CO₂ saturated densities were calculated using the pure densities and corrected using the partial molar volume as described by Garcia [24].

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

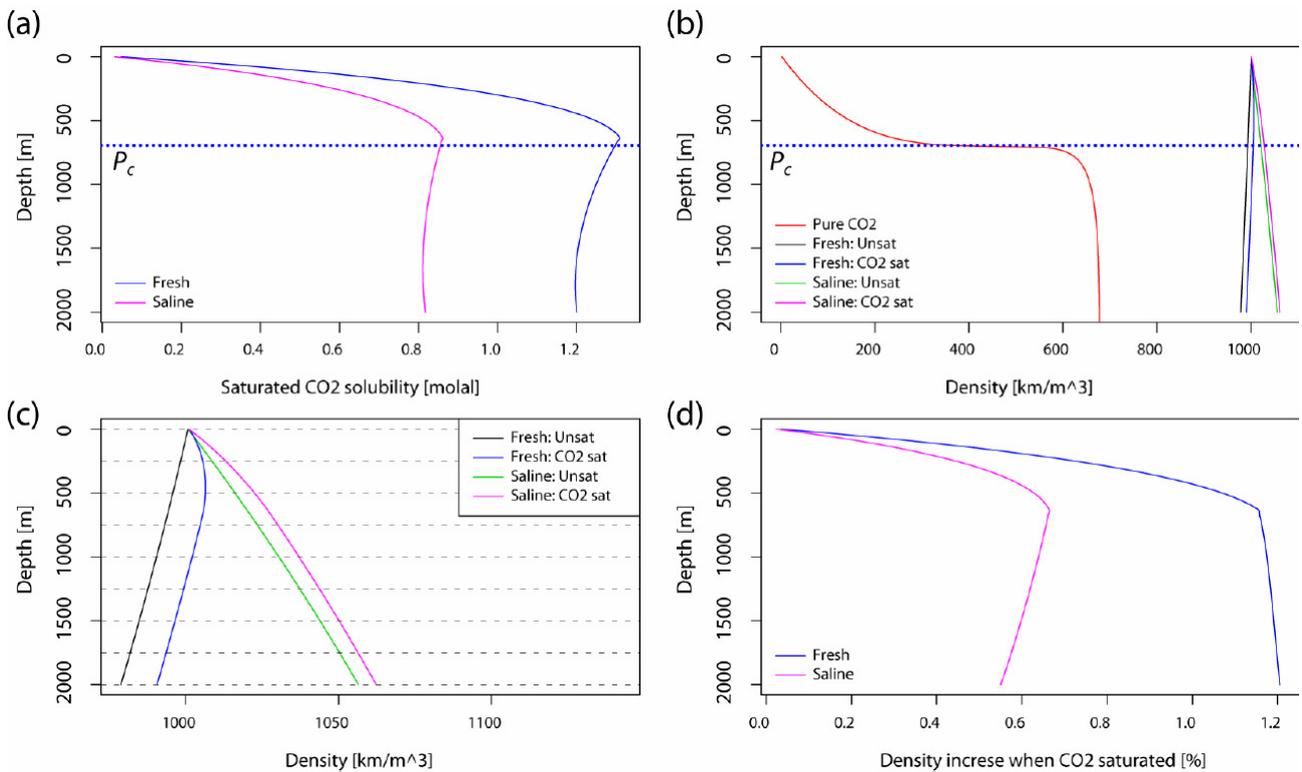


Fig. 3. Downhole properties of pure CO₂, pure fresh water, brine, CO₂ saturated fresh water and CO₂ saturated brine. (a) Solubility of CO₂ in fresh water and brine, (b) density of pure CO₂ and fluids, (c) zoom in on the fluid densities and (d) percentage increase in fluid density as a consequence of saturating the pure fluid with CO₂. Salinity increases with depth at 1 mol/l/km.

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 [28] 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 \gg 800m to ensure that the CO₂ is in the dense phase.

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 Figure 4. The standard approach could be done by injection of CO₂ into an aquifer. Dense phase CO₂ has a density \sim 700kg/m³, leaving a density difference between the CO₂ and formation fluids \sim 300kg/m³ (Fig. 3b) which drives the buoyant migration of CO₂ towards the top of a reservoir layer. This technique is reliant on the presence of a caprock with a capillary entry pressure sufficient to hold the CO₂.

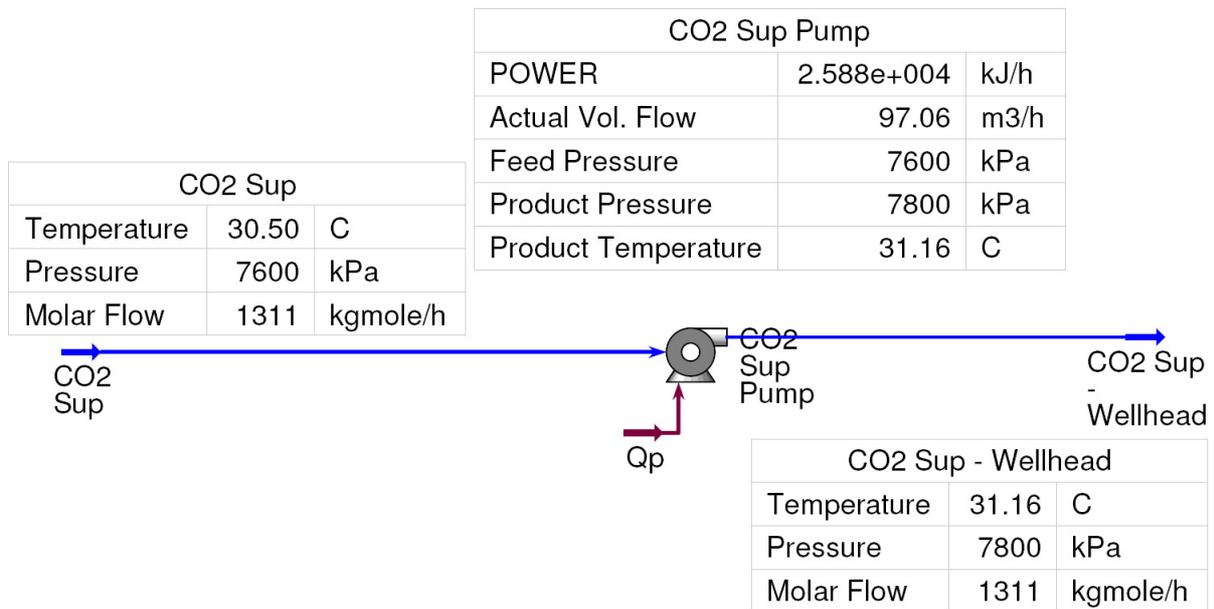


Fig. 4. Standard injection process simulation PFD

Option 2: CO₂-brine surface mixing strategy

CO₂-brine surface mixing and injection method is an important and perhaps an essential step for the secure storage of CO₂ as it removes buoyant vertical migration in the reservoir. For example, once the CO₂ is dissolved in brine, it will no longer migrate upwards 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 done 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 previous finding [29] which suggest 90% dissolution of static CO₂ into brine in nine minutes between a pressure ranges of 330 to 580 psia. We estimate tank residence time of four minutes for the CO₂-brine dissolution and such operating condition requires reasonable temperature and pressure. 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 the temperature of 30.20 °C, pressure of 1088 psia (7499 KPa or 74.99 bar). The brine stream also enters with similar pressure but less temperature (22.39 °C and 1092 psia (7526 KPa)). This method proves to be efficient as the simulation result show that greater pressure and lower temperatures increases solubility in the mixing vessel. Due to the phase behaviour of CO₂ stream, the mixing operation requires minimum pressure of 7433 KPa (1078 psia) which is the critical pressure of CO₂. The facilities design and simulation results of this study show pressure below CO₂ critical pressure to be 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 operating temperature and pressure of the mixing vessel which has 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 behaviour of the mixing vessel product (CO₂-saturated brine steam) (Fig. 5)) is quite strange and care should be taken in the design of the facilities and operation of the stream. The stream behaviour is relatively different from supercritical CO₂ stream but closer to the brine stream. This great influence of the product stream towards brine stream is closely linked with high boiling point of brine as shown in figure 5. The flow rate of CO₂ stream used in the design is 1311 kgmole/h (based on 5×10^5 tonne (11,484,360 kgmole) of CO₂ /year) and flow rate of brine is 2515 kgmole/h (Fig. 6). Due to the low solubility of the CO₂ in the brine, a large volume of brine is necessary to dissolve a given amount of CO₂. 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 ten times higher than the flow rate of CO₂. However, less brine flow rate is possible with higher pressure vessel. The operating condition of

the mixing vessel can be optimized to save cost and hence could be different from other surface process facilities. Considering the above proposed CO₂/brine flow rates and residence time, the size of cylindrical mixing vessel required to handle such volume is about 4.0m x 12.3m (diameter x height respectively) (estimated with cylinder volume equation [30], $V = 0.7854d^2h$ 6). Considering the large size of this pressure vessel, multiple vessels with smaller diameter is suggested as more viable process capabilities. The pressure mixing vessel is the most important unit operations 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 analysing the surface mixing vessel, much more detailed work on the physical equipment and the costings still needs to be undertaken. A description of the conceptual CO₂-brine surface mixing and injection strategies with process flow diagram showing pipeline segment is found in Figure 6.

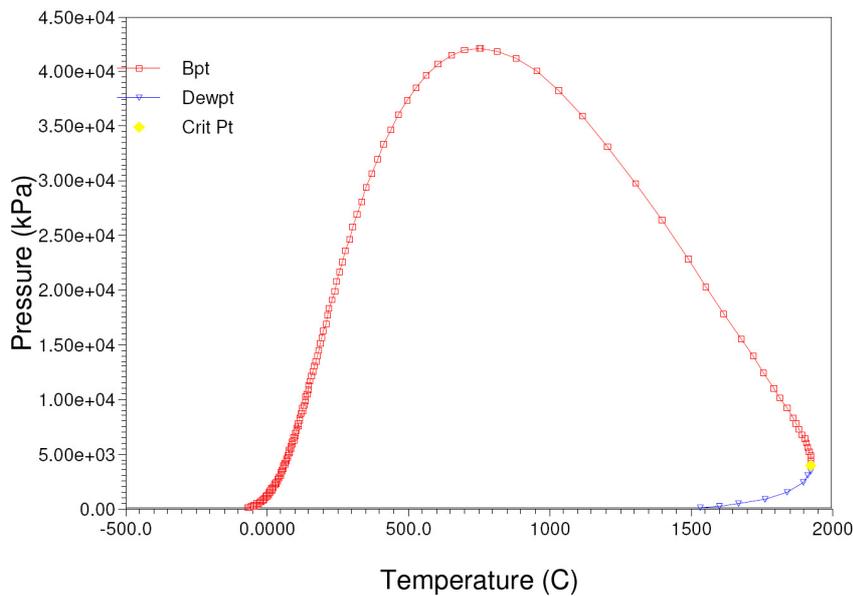


Fig. 5. CO₂-saturated brine stream phase envelope

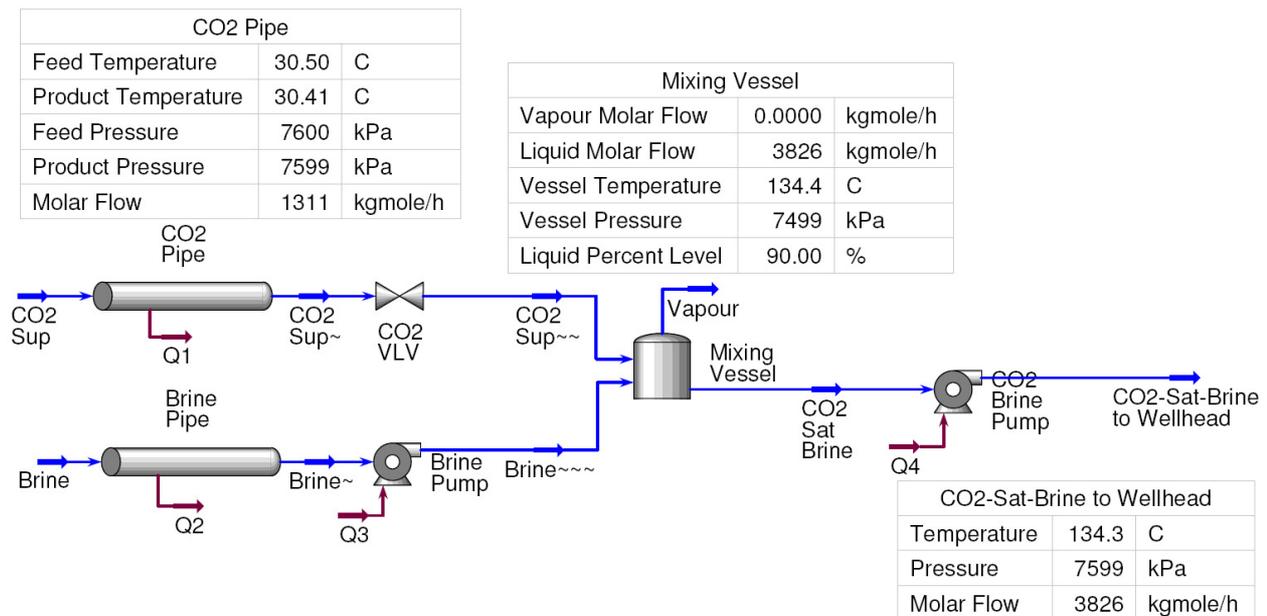


Fig. 6. CO₂-brine surface mixing process simulation PFD

In order to operate the mixing strategy in the pressure mixing vessel, the brine and the carbon dioxide is brought up to the 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 or greater than 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 lower pressure in a controlled manner to suit the pressure required in the mixing vessel. The mixing pressure should normally be the range needed for injection but could be step up or down as required to be equal to wellhead pressure and the range is dependant on the storage formation condition.

The simulation provides functions that allow stream rate, velocity in the pipeline or a vessel temperature or pressure, etc. 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. 7, Tables 2 and 3) show the behaviour of streams as well as flow performance. The size of pipeline depends on the amount of materials handled and the distance of 600m from the surface injection facilities (onshore storage site) to wellhead is proposed because the injection facilities should be close to injection wellhead (Table 2) but could be more distant in case of 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 the streams experience in the mixing vessel are very important as the dissolution of CO₂ in brine and hydrate formation depends on that.

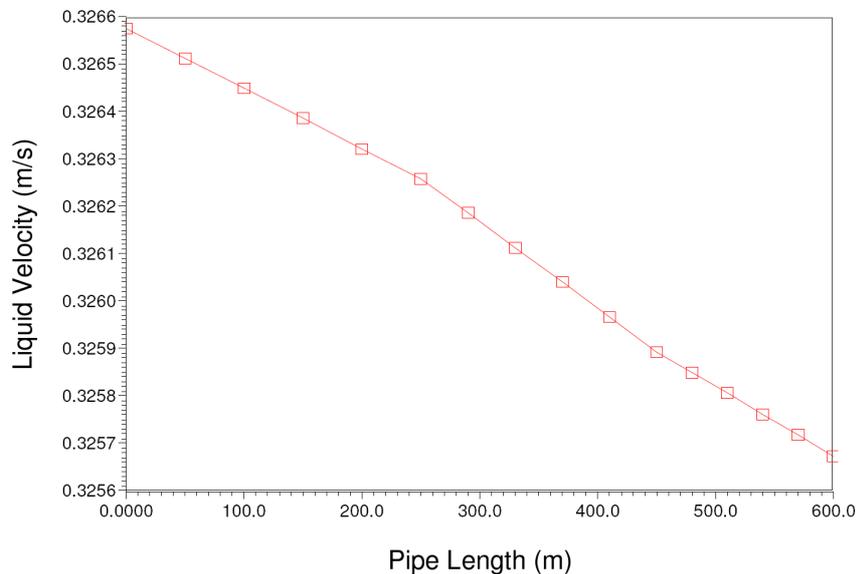


Fig. 7. Liquid Velocity across the pipeline

Table 2 Pipeline sizing parameters

PARAMETERS				
Pressure Gradient/Pipe Parameters				
Pipe Flow Correlation	Beggs and Brill		Pressure Drop: 0.9792 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)	304.8	304.8	304.8	
Outer Diameter (mm)	323.8	323.8	323.8	
Inner Diameter (mm)	303.2	303.2	303.2	
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 *	

Table 3 Pipeline segment profile and operating conditions

HEAT TRANSFER					
Heat Loss:	2.892e+004 kJ/h	Ambient Temp:	0.5000 C *	Overall HTC:	1.507 kJ/h-m ² -C
Inside Heat Transfer Coefficient Estimation					
Include Inner HTC:	Enabled	Correlation:	Profes		
Pipe Wall Resistance Estimation					
Include Pipe Wall Resistance:	Enabled				
Insulation Resistance Estimation					
Include Conduction:	Disabled	Type:	Urethane Foam	Thermal Cond.:	1.800e-002 W/m-K *
				Thickness:	1.000e-002 m *
Outside Heat Transfer Coefficient Estimation					
Include Outer HTC	Ambient Medium	Ground Type	Ground Conductivity	Buried Depth	
Enabled	Ground	Dry Peat	0.1700 W/m-K *	1.000 m *	
PROFILES					
Data					
Distance (m)	Elevation (m)		Increments		
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	3.600	
Pressure (kPa)	8000	7992	7984	7976	
Temperature (C)	32.00	31.98	31.95	31.93	
Heat Transferred (kJ/h-m)	---	48.25	48.22	48.18	
Flow Regime	Liquid Only	Liquid Only	Liquid Only	Liquid Only	
Liquid HoldUp	1.000	1.000	1.000	1.000	
Friction Gradient (kPa/m)	6.553e-003	6.553e-003	6.553e-003	6.553e-003	
Static Gradient (kPa/m)	0.1545	0.1545	0.1545	0.1545	
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000	
Liq. Reynolds	2.641e+006	2.638e+006	2.635e+006	2.633e+006	
Vap. Reynolds	---	---	---	---	
Liquid Velocity (m/s)	0.6690	0.6690	0.6690	0.6689	
Vapour Velocity (m/s)	---	---	---	---	
Deposit Thickness (mm)	---	---	---	---	
Deposit Volume (m ³)	---	---	---	---	
Length (m)	200.0	250.0	290.0	330.0	
Elevation (m)	4.800	6.000	4.700	3.400	
Pressure (kPa)	7968	7960	7968	7976	
Temperature (C)	31.91	31.88	31.90	31.92	
Heat Transferred (kJ/h-m)	48.15	48.11	48.14	48.16	
Flow Regime	Liquid Only	Liquid Only	Liquid Only	Liquid Only	
Liquid HoldUp	1.000	1.000	1.000	1.000	
Friction Gradient (kPa/m)	6.552e-003	6.552e-003	6.551e-003	6.550e-003	
Static Gradient (kPa/m)	0.1545	0.1545	-0.2093	-0.2093	
Accel. Gradient (kPa/m)	0.0000	0.0000	0.0000	0.0000	
Liq. Reynolds	2.630e+006	2.627e+006	2.629e+006	2.630e+006	
Vap. Reynolds	---	---	---	---	
Liquid Velocity (m/s)	0.6689	0.6689	0.6688	0.6687	
Vapour Velocity (m/s)	---	---	---	---	
Deposit Thickness (mm)	---	---	---	---	
Deposit Volume (m ³)	---	---	---	---	

Complete dissolution of CO₂ in brine is considered as significant impact strategy because they would influence engineering considerations for design and operation of CO₂ injection wells. This tests 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 (Fig. 3c and d) and hence has a downward buoyancy drive. This is a significant advantage since it removes the need for a perfect seal and can be injected safely at shallower depths than the pure CO₂. Further, the production of brine from deeper depths within the reservoir would induce a pressure drawdown which enhances the migration of the CO₂ saturated brine away from the injection site whilst providing a mechanism to regulate the reservoir pressure. This appears to be a promising option, which 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 geological formation may assist transformation into carbonate minerals (equations 2 to 5) [9]. This injection strategy investigates possibility of enhancing the process by doing 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 varies and may reach several hundred bar. Dense CO₂ is mixed with water in surface facilities prior to injection into geological formation (Fig. 8). 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.

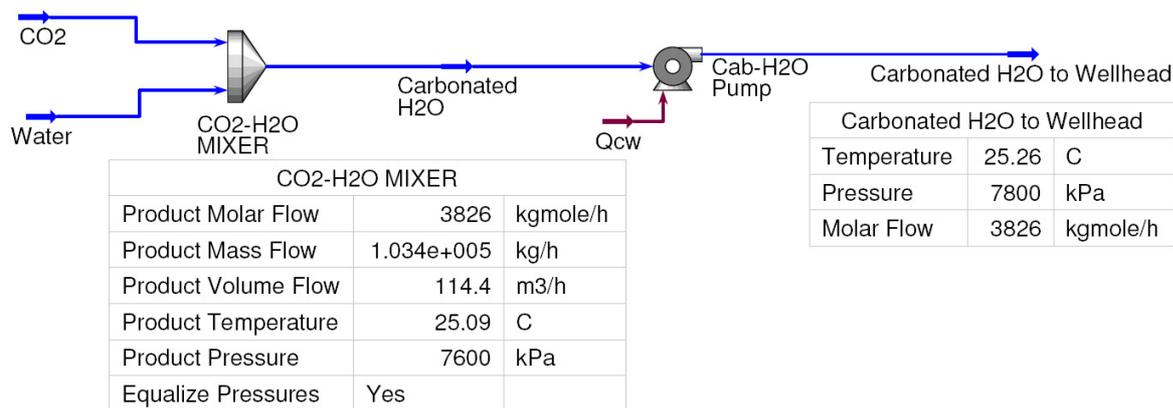


Fig. 8. CO₂-water surface mixing process simulation PFD

When CO₂ dissolves in water, it forms a carbonic liquid that is less dense than the expected ambient saline formation fluid (by ~50kg/m³ for the parameterisations chosen here and at reservoir depths, Fig. 3c), hence an upward potential flow rise is expected. However, this density difference is an order of magnitude less compared to supercritical CO₂. The use of sea water 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 for the standard injection of pure CO₂) into the formation. Since 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 decreases beneath the critical pressure. In summary, this does not appear to be a good option. The simulation result show that free water is found in the carbonated water stream and hydrate is formed at the moderate temperature of 10°C. These conditions make handling of 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 but inhibitor could be added in carbon steel pipes to reduce the impact of corrosion as suggested by Cosham [26], and previously discussed under materials considerations above. We recommend that corrosion preventive actions be evaluated and implemented which includes choosing correct operating conditions and corrosion resistant materials. The best construction materials recommended for use in this type of process is 304/316L stainless steel which is proved to be the best corrosion resistance.

Option 4: CO₂ alternating brine (CAB) injection strategy

Operation strategy that alternates supercritical CO₂ with brine injection is simulated. In this method, the supercritical CO₂ and brine are alternately injected (Fig. 9). This strategy is based on water alternating gas (WAG) model. The model involves two standard injection facilities with one pumping CO₂ stream and the other 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 underway elsewhere in the CASSEM project to explore the effects of this strategy in CO₂-brine pore scale mobility and predictions of the changes to capillary forces, residual saturation, and density of injected fluids (CO₂ alternating brine) relative to reservoir fluids.

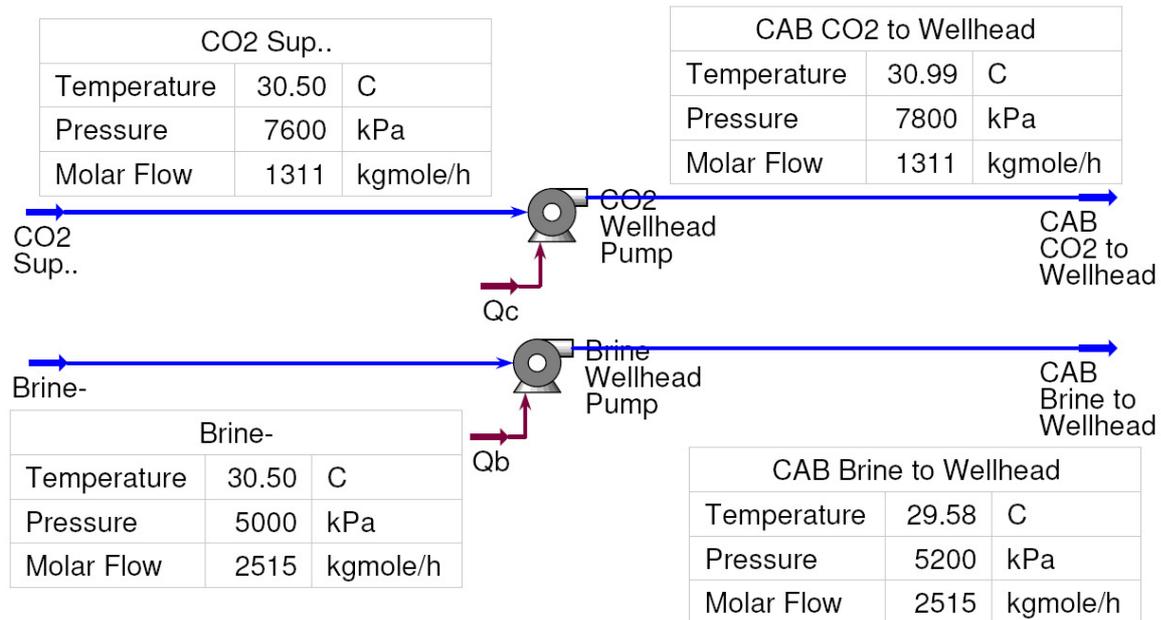


Fig. 9. CO₂ alternating brine process simulation PFD

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 basis for determining whether further work should be done on the proposed process. The interaction of supercritical CO₂ stream with other streams (brine and water) and their behaviour in the process facilities were predicted in various operating conditions relevant to geological formations. The injection of a saturated CO₂-brine stream studied here demonstrates that surface dissolution facilities enhanced CO₂-brine solubility and directly improves CO₂ sequestration.

The findings show that dissolving CO₂ into brine at the surface facilities prior to injection into geologic formations produces CO₂-saturated-brine stream with density slightly higher than original brine in the formation. The denser CO₂-saturated-brine stream when injected to the formation is capable of eliminating the buoyancy force which is a strong driving force to bring CO₂ to the surface. Moreover, CO₂-brine surface dissolution prove to be the primary strategy to speed up CO₂ immobilization as the period of time needed to achieve immobilization in the subsurface formation is enhanced by the surface mixing vessel. Immobilized CO₂ will remain indefinitely even if the integrity of the seal is not intact. No additional time is required for immobilization after injection ends. Thus, CO₂-brine surface mixing strategy is recommended because it is directly linked with enhancement and secure storage of CO₂ in geologic formations. It is clear that CO₂-brine surface mixing and injection is best of the four injection strategies considered in this study. Mobile dense phase CO₂ is dependent of the integrity of 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 handlings.

There is a need for further research to address gaps in our knowledge about large scale CO₂ interaction and behaviour in the surface facilities and subsurface formations. Further studies are underway 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 as well as underpin the impact of impurities in the equipments.

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