Solving the carbon-dioxide buoyancy challenge: The design and field testing of a dissolved CO₂ injection system

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Abstract

Long-term security is critical to the success and public acceptance of geologic carbon storage. Much of the security risk associated with geologic carbon storage stems from CO₂ buoyancy. Gaseous and supercritical CO₂ are less dense than formation waters providing a driving force for it to escape back to the surface via fractures, or abandoned wells. This buoyancy can be eradicated by the dissolution of CO₂ into water prior to, or during its injection into the subsurface. Here we demonstrate the dissolution of CO₂ into water during its injection into basalts leading directly to its geologic solubility storage. This process was verified via the successful injection of over 175 tons of CO₂ dissolved in 5000 tons of water into porous rocks located 400-800 m below the surface at the Hellisheidi, Iceland CarbFix injection site. Although larger volumes are required for CO₂ storage via this method, because the dissolved CO₂ is no longer buoyant, the storage formation does not have to be as deep as for supercritical CO₂ and the cap rock integrity is less important. This increases the potential

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storage resource substantially compared to the current estimated storage potential of supercritical CO₂.

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1. Introduction

The safe long-term storage of anthropogenic carbon has been widely advocated to limit the CO₂ concentration of the atmosphere (e.g. Bachu and Adams, 2003; Bachu, 2008; Holloway, 2001, Oelkers and Schott, 2005; Oelkers and Cole, 2008; Van Noorden, 2010, Shaffer, 2010). If stored as a supercritical fluid, in excess of 35 km³ of storage volume would be required annually to stem the anthropogenically induced augmentation of CO₂ concentration in the atmosphere (IPCC, 2005; Benson and Cole, 2008). Best suited for this purpose are large subsurface rock formations including sedimentary basins, depleted oil and gas reservoirs, coal beds, and basalts due to their large volume and pervasive availability (IPCC, 2005; Orr, 2009). The typical method to inject CO₂ into these subsurface rock formations is as a single phase. Once injected into these subsurface formations, carbon storage proceeds through a sequence of four trapping mechanisms: structural/stratigraphic trapping, residual trapping, solubility trapping, and mineral trapping (Benson and Cole, 2008). This sequence, as outlined in Fig. 1a, suggests that the trapping of gaseous or supercritical CO₂ is dominated by structural/stratigraphic trapping for at least the first 10 to 100 years. This trapping mechanism relies on an impermeable cap rock to hold buoyant gaseous and/or supercritical CO₂ in the subsurface. Residual trapping occurs only when the CO₂ concentration is sufficiently low such that it becomes immobile in pore spaces. Estimates suggest that, if injected as gaseous or supercritical CO₂, more than 10 to 1000 years are required before it is dissolved and longer for some of it to be incorporated into mineral phases, permanently immobilizing the injected CO₂ (Xu et al., 2004).

The largest risk of geologic carbon storage is believed to be leakage of the carbon either into the atmosphere or into overlying fresh-water aquifers (e.g. Wilson et al., 2003; Burton and Bryant, 2009a, b; Celia et al., 2009; Kharaka et al., 2009; van der Zwaan and Gerlagh, 2009; Little and Jackson, 2010; Lu et al., 2010). Leakage may be promoted by the presence of abandoned wells (Gasda et al., 2004; Nordbotten et al., 2005), or fluid-caprock interaction (Gaus, 2010; Fitts and Peters, 2013). Much of this risk is eliminated once the

injected CO₂ is dissolved into the aqueous phase, as CO₂ saturated water is denser than CO₂-free water (Teng et al., 1997; Bodnar et al., 2013). This project was designed to dissolve CO₂ into water during its injection to overcome the risks associated with the presence of buoyant CO₂ gas or supercritical fluid in the subsurface through the design and field testing of a novel CO₂ injection system. The purpose of this communication is to describe this injection system and to report on its successful field test.

2. RESULTS AND DISCUSSION

Carbon-dioxide injection was performed at the CarbFix injection site in Hellisheidi, Iceland (Gislason et al., 2010; Matter et al., 2009; 2011; Aradottir et al., 2011; Gislason and Oelkers, 2014). This injection site is situated about 3 km south of the Hellisheidi geothermal powerplant, 25 km east of Reykjavik. The powerplant currently produces 40,000 tons of CO₂ per year. The CO₂ gas is a by-product of geothermal energy production and is of magmatic origin. In this pilot study, pure CO₂ pumped from a geothermal well in the vicinity was purchased and transported to the site. This CO₂ was co-injected into well HN-2, with water collected from well HN-1 located 1.5 km from the injection well. The composition of this water and an overview of the injection site are reported by Alfredsson et al. (2013). The injection well is 2000 m deep and is surrounded by 12 monitoring wells ranging in depth from 150 to 1300 m. The injection well is cased to a depth of 400 m and open to the rock formation below. The rocks at the Hellisheidi injection site are of ultramafic to basaltic composition (Alfredsson et al., 2013). The target injection formation is highly permeable with lateral and vertical intrinsic permeabilities estimated to be 300 and 1700 $\times 10^{-15}$ m², respectively and porosity of 8.5% (Aradottir et al., 2012). It is located at a depth of 400-800 m below the subsurface, and consists of basaltic lavas and glassy hyaloclastites (Alfredsson et al., 2013). The dominant formation waters at this depth have temperatures from 18 to 33 °C and are oxygen poor. The pH of these waters range from 8.4 to 9.4; the partial pressure of CO₂ is below that of the atmosphere.

Due to the risk of CO₂ escape to the atmosphere through the basaltic rock fracture network at CarbFix injection site, efforts were made to inject it in dissolved form. To dissolve carbon-dioxide into water during its injection the CO₂ to H₂O ratio must be lower than the CO₂ solubility at the temperature and pressure of the target storage rock formation. Target injection rates of 70 and 1940 g/s were selected for CO₂ and H₂O at the Hellisheidi site such that the overall concentration of CO₂ was below its solubility in the well at its release

point. If completely dissolved, the resulting injection water would have a CO₂ concentration of 0.823 mole kg⁻¹ dissolved inorganic carbon (DIC) and a pH equal to 3.85 at 20°C according to mass balance and chemical speciation calculations (Parkhurst and Appelo, 1999). Carbon dioxide for the injection was supplied from a 30 m³ reservoir tank. The pressure in this reservoir tank was maintained at 26-28 bars by a pressure control valve, which sends liquid CO₂ from the base of the tank to a stainless steel evaporator feeding CO₂ gas to the top of the tank. Gas flow from the tank was maintained between 55-70 g s⁻¹ through a needle valve by boiling the required amount of liquid CO₂ with a separate evaporator. Co-injected water was supplied from an adjacent well and pumped into a 27 m³ reservoir tank filled with polypropylene balls (Allplas, RITTER Chemie GmbH) to prevent gas exchange between the water and atmosphere during its storage. The maximum residence time of the water in the tank was less than four hours. From the storage tank the water flowed by gravity towards the injection site at maximum delivery pressure at the wellhead at 1.5 bar, thus arresting the injection if substantial well clogging occurred. A Metso DN25 control valve supplied water to the injection well in the selected fixed mass ratio to the CO₂ gas stream.

The design of the injection system is shown in Fig. 2. The CO₂ and H₂O are injected via separate polybutylene and polyethylene pipes, respectively, to a depth of 330 to 360 m. At this depth, CO₂ is released via a sparger into the flowing H₂O. The sparger consisted of a 0.67 m long 316L stainless steel pipe with the lowest 0.57 m containing 54 spirally aligned 1 mm holes, ensuring release of sufficiently small gas bubbles so that they are carried in the water stream to greater depths in the well. The mixture is carried from the sparger via a polyethylene mixing pipe extending down to 540 m where it is released to the subsurface rocks. A Kenics, 1.5-KMS-6 static mixer is located at a depth of 420 m to aid CO₂ dissolution.

The temporal variation of injected CO₂ and H₂O during the test of this injection system is shown in Fig. 3. Overall, 175 tons of CO₂ were injected into the subsurface in dissolved form together with approximately 5000 tons of H₂O from 15 to 17 March 2011 and 10 January to 15 March 2012. The typical fluid injection rate was 1800 g s⁻¹. Mass balance calculations indicate that the average residence time of the CO₂-H₂O fluid in the well from the sparger to a depth of 540 m was 4 minutes and 30 seconds. Verification of the complete dissolution of CO₂ during its injection was performed by digital downhole camera and by high-pressure well water sampling using a custom made bailer (Alfredsson et al., 2011). A detailed description of the sample treatment procedure is provided by Alfredsson et al. (2011). Briefly, once the bailer was on the surface, it was connected to a high pressure sampling line maintaining the pressure of the 480 m sampling depth for pH measurement using a Coor Instruments high P/T electrode. A portion of the sample was passed through a sample loop (of known size) against a backpressure regulator to prevent boiling of the sample. The fluid in the sampling loop was degassed to ambient pressure into a syringe containing strong base to collect CO₂ for titration analysis. Digital images were taken using a downhole camera (CCV Engineering & Manufacturing Inc., WC1750 slimline waterwell inspection camera) on 16 March 2011 at depths from 90 to 550 m. The camera was located in the service pipe (Number 7 in Fig. 2), outside of the fluid-mixing pipe (number 4 in Fig. 2), so that it images the fluid after CO₂ mixes with water but before it enters the target rock formation. Resulting images, such as presented in Fig. 4 show the well fluid to be void of gas bubbles consistent with the complete dissolution of CO₂ 1.5 m above the fluid outlet at 540 m as the fluid flows towards the main feed zone at 525 m (Video 1 in supplementary material). To confirm the ability of this camera system to visualize gas bubbles, Fig. 5 (Video 2 in supplementary material) shows exsolution of CO₂ gas in the injection well water as the camera was moved to the groundwater table at 93 m following an injection period where the CO₂/H₂O mass ratio was not low enough to complete CO₂ dissolution. This led the excess CO₂ gas to rise towards the surface through the water column. In total 11 fluid samples were obtained from a depth of 530 m during the test injection performed during 2012; the sampling dates are shown in Table 1. Each of these fluid samples were analyzed for total dissolved inorganic carbon and 6 of the 12 were measured for *in-situ* pH. As shown in Fig 3 and Table 1, in each case the dissolved inorganic carbon concentration of the sample fluid was on average within 5% of the 0.82±2% mol/kg concentration based on measured CO₂ and H₂O mass flow rates into the well and the fluid pH was 3.89±0.1 confirming the complete dissolution of the CO₂ during its injection.

If injected into the subsurface as a dissolved phase, CO₂ is far less likely to escape back to the atmosphere due to its lack of buoyancy (Gilfillan et al., 2009). Some buoyancy risks nevertheless remains; the physics of buoyancy leakage has been discussed in detail by Huppert and Neufeld (2014). If the CO₂ charged injection water depressurizes below its equilibrium partial pressure or if the temperature increases above its solubility limit, CO₂ could exsolve creating a buoyant CO₂-rich phase. Exsolution occurs when the fluid pressure is less than the partial pressure of the dissolved CO₂. The depth required for this pressure depends on the height of the water column, the dissolved CO₂ concentration, the fluid composition, and the existence of any overpressure. As such, the depth at which exsolution could occur is strongly site dependent. The risks of exsolution, however are mitigated by 1) the fact that CO₂-rich H₂O is denser than CO₂-poor H₂O (Teng et al., 1997; Bachu and Adams, 2003) and 2) water-rock interaction/fluid mixing. The dissolution of aluminosilicate, divalent metal silicate, and carbonate minerals, into the reactive, acidic CO₂ charged injection waters will increase the pH of this fluid. If the fluid pH rises above 6, the equilibrium CO₂ partial pressure of the fluid will decrease substantially due to aqueous bicarbonate species formation (MacKenzie and Anderson, 2013; Alfredsson et al. 2013; Bodner and Yardley, 2014). Furthermore, in many instances the dissolution of divalent metal silicate minerals in CO₂-charged injection waters can lead to the precipitation of stable carbonate minerals, and thus *in-situ* mineral storage (Oelkers et al., 2008; Matter et al., 2009). Similarly, the dilution of CO₂ through the mixing of the injection water with formation water will further stabilize the combined aqueous phase.

The injection of CO₂ into the subsurface in dissolved form increases substantially the mass of fluid to be injected during subsurface CO₂ storage efforts. The water demand as a function of pressure is shown in Fig. 6; the mass of water required at 25°C to dissolve 1 kg of CO₂ decreases from 665 kg to 10 kg of H₂O with increasing pressure from 1 to 64 bars (Orr 2009); the total water required for upscaling this CO₂ injection method can be estimated by multiplying the water demand shown in Fig. 6 by the mass of CO₂ to be stored. Although this quantity of H₂O is substantial, massive quantities of H₂O are currently being injected into the subsurface worldwide. It is estimated that over 3 Gt/yr of oil field brines are brought to the surface in the United States and the United Kingdom alone (American Petroleum Institute, 2000; Department of Energy and Climate Change of the United Kingdom, 2009); the main disposal strategy of these brines is their reinjection. Re-injecting these brines charged with

CO₂ at 60 bar would dissolve approximately 2% of the global annual CO₂ emissions and require ~3.64 km³ storage volume. If all current global anthropogenic CO₂ emissions were stored via the method described in this report, from 330-1700 km³ year⁻¹ in storage volume would be required. This compares to just ~40 km³ year⁻¹ for injecting supercritical CO₂ into the subsurface. However, because the CO₂ is no longer buoyant, the storage formation does not have to be as deep as for supercritical CO₂ and the cap rock integrity is less important. This increases the potential storage resource substantially compared to the current estimated storage potential of supercritical CO₂.

Although the dissolution of CO₂ into water during injection does not change the total mass of H₂O required for solubility storage – *in-situ* solubility storage requires an identical quantity of fluid – some additional challenges arise. The need to inject larger quantities of fluid could lead to pressure build-up in the target aquifers if sufficient transmissivity is not available and may increase storage costs due to the need to increase the number of injection wells. This increased pressure could lead to increased seismic activity and thus an increased risk of CO₂ leakage (Nicol et al., 2011; Frohlich, 2012; Mazzoldi et al., 2012; Zoback and Gorelick, 2012; Gan and Frohlich, 2013; Kim, 2013; McGarr, 2014). Pressure build-up, however, can be avoided by using formation water obtained from the target aquifer for the injection itself (Burton and Bryant, 2009a). In instances where insufficient fresh water is available for the dissolution of CO₂ during its injection, seawater could be substituted in coastal areas. The solubility of CO₂ in seawater is comparable to that of freshwater and it is abundant near the coasts, adjacent to sub-ocean basalt formations with sufficient storage capacities to accommodate vast quantities of injected CO₂ (Goldberg et al., 2008; Wolff-Boenisch et al., 2011).

The energy required to inject CO₂ as a dissolved phase in water depends only mildly on the depth of the target storage formation. As the target formation depth increases, the required compression increases but the water demand decreases. As a result, the electrical energy required to co-inject CO₂ with water remains fairly constant with depth at ~100 kWh/ton CO₂ stored – see Fig. 6. The energy penalty of this injection method depends on the type and efficiency of the power plant. The Hellisheidi power plant emits 21.6 g of CO₂ per kWh of electricity produced (Gunnlaugsson et al., 2012). In contrast, CO₂ emissions from typical coal and gas fired power plants range from 385 to 1000 g of CO₂ per kWh electricity

produced (IPCC, 2007). Thus the energy penalty associated with injecting CO₂ as a dissolved phase into the subsurface is on the order of 0.2% for the case of the Hellisheidi power plant and ranges from 3 to 10% for typical coal and gas-fired power plants. The total cost of injecting CO₂ as a dissolved phase depends strongly on the cost of the energy used for the injection and power plant efficiency. Nevertheless, as emphasized by Gislason and Oelkers (2014) the overall cost of carbon capture and storage (CCS) is currently dominated by the cost of capture. For the case of the injection at Hellisheidi, dissolved CO₂ injection will add less than 10% to the overall cost of CCS once the process is fully upscaled.

The dissolution of CO₂ into H₂O during its injection into the subsurface increases geologic carbon storage security by avoiding the need to rely on structural/sedimentary trapping mechanisms. By passing directly to solubility trapping during injection, the geologic storage trapping mechanism sequence simplifies to that shown in Fig. 1b. Geologic storage will be dominated by solubility trapping until a time when mineral trapping may occur. The degree to which mineral trapping occurs and the time required will depend on the identity of the host rock and the availability of the divalent metal cations required for carbonate mineral precipitation (Aradottir et al., 2012; McGrail et al., 2006; Wolff-Boenisch et al., 2006; Oelkers et al., 2008; Matter and Kelemen, 2009; Gislason et al., 2010). As such, Fig. 1b is illustrative rather than quantitative. Regardless of the rate and extent of mineral trapping, the dissolution of CO₂ during its injection will enhance storage security associated with the presence of buoyant gaseous or supercritical carbon dioxide in the subsurface. This increased storage security through the injection of dissolved CO₂ could 1) enhance public acceptance of geologic storage on land near existing power stations and population centers, and 2) make possible subsurface carbon storage in regions where sedimentary basins with impermeable cap rocks are not available.

3. Conclusion

The results summarized above demonstrate the possibility to dissolve CO₂ into water during its injection onto the subsurface, leading to its solubility storage within 5 minutes. Solubility storage holds two major advantages that can enhance public acceptance and storage security. First, as CO₂-saturated water is denser than CO₂-free water, solubility storage limits potential leakage. Second, the dissolution of CO₂ into water can promote the carbonation of the host rocks if they contain sufficient divalent metals. These advantages, however, need to be weighed against the potential for increased seismic risk, and the additional energy and water required for injection. As such, the dissolved CO₂ injection system described above will

be most favorable for injection into reactive fractured rocks such as basalts and ultramafic rocks, and in rock formations having questionable caprock integrity (e.g. caprocks containing abandoned wells).

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- a) Calculated from the measured CO₂ and water mass flow.
 b) pH measured at *in-situ* conditions (20 °C and ~ 38 bars).

Figure 1. Schematic illustration of the contribution of various trapping mechanisms to the

time a) injection of gaseous or supercritical CO₂, b)

Note the time required for mineral trapping is
 dissolved CO₂ in b.

Figure 2. Design of the carbon-dioxide injection system. Natural water level in well is 80-90 m below the surface. 1) CO₂ injection pipe, 2) water injection pipe, 3) CO₂ sparger located at a depth of 330-360 m, 4) outer mixing pipe extending to a depth of 540 m, 5) Mixer at 420 m, 6) fluid outlet at 540 m, 7) service pipe for downhole sampling and observations, 8) service entry to well head space.

Figure 3. Temporal variation of CO₂ (red curve) and water (blue curve) flow rates of the injected fluid, calculated dissolved CO₂ concentration, and measured fluid pH (open circles) and dissolved CO₂ concentration (filled circles) at the CARBFIX injection site in Hellisheidi Iceland from 15 March to 17 March 2011 and 28 January to 11 March 2012. Gas and water pressures at the wellhead were between 20-25 bar and 0.5-1.5 bar during injection.

Figure 4. Image taken at a depth of 538.5 m in the injection well at 16:00 16 March 2011. The camera enters the injection well through the service pipe (7 in Fig. 2). At this time the CO_2 and H_2O inlet flows were 27.1 and 750 g/s, respectively. No CO_2 bubbles are visible consistent with the complete dissolution of CO_2 during its injection (see text). The complete video from which the image was obtained is presented in the electronic supplement.

Figure 5. Series of images taken using a CCV Engineering & Manufacturing Inc., WC1750 slimline waterwell inspection camera as a function of depth on 16 March 2011. The camera

enters the injection well through the service pipe (7 in Fig. 2). At this time the CO_2 and H_2O inlet flows had been terminated due to incomplete dissolution of CO_2 in the H_2O . The camera was orientated facing downwards. Images were taken as the camera was being raised towards the ground water table. No CO_2 bubbles are visible at depth, but an increasing concentration of bubbles are present as one approaches ground water table, illustrating how this camera can successfully identify the presence of gas bubbles. The complete video from which the images were obtained is presented in the electronic supplement.

Figure 6. Calculated water demand and energy requirement for the injection of one ton of CO_2 dissolved in water as a function of injection pressure. Energy requirement was estimated from combining the estimated gas compressor size based on rate and suction and discharge pressure range with measured power requirement of the water pumps used in the CarbFix experiment. The water demand at each pressure was based on the solubility of CO_2 in water at 20°C according to Henry's law (Wannikhof, 1992) and therefore gives the minimum water needed to maintain all CO_2 dissolved at a given injection pressure.

Electronic supplement. Two videos from which the images shown in Figures 4 and 5 were obtained.

Table 1. Selected chemical characteristics of injection waters.

	Time	CO ₂ mass flow (g s ⁻¹)	Water mass flow (g s ⁻¹)	DIC _{calc} calculated (mol/l) ^a	DIC _{meas} from Bailer sample (mol/l)	T of bailer sample	pH ^b
Date							
25.01.2012	09:30-11:30	18.5	515	0.82	0.72	16.9	
31.01.2012	09:30-11:30	23.5	653	0.82	0.83	17.7	
03.02.2012	12:05-14:05	49.1	1363	0.82	0.94	21.1	
06.02.2012	09:45-11:45	58.0	1612	0.82	0.84	21.1	
09.02.2012	09:30-11:30	63.2	1755	0.82	0.86	18.9	
13.02.2012	09:20-11:20	37.2	1034	0.82	0.85	18.8	
16.02.2012	09:30-11:30	66.3	1843	0.82	0.86	21.6	
20.02.2012	09:30-11:30	60.1	1671	0.82	0.89	21.4	3.88
23.02.2012	09:40-11:40	62.2	1728	0.82	0.89	21.5	3.99
28.02.2012	09:30-11:30	64.6	1794	0.82	0.83	21.7	3.87
02.03.2012	09:15-11:15	60.5	1682	0.82	0.87	21.1	3.89
05.03.2012	09:05-11:05	56.3	1563	0.82	0.88	21.5	3.83
08.03.2012	09:25-11:25	41.8	1161	0.82	0.9	19.9	3.88

c)

d)