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Rapid solubility and mineral storage of CO₂ in basalt

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Abstract

The long-term security of geologic carbon storage is critical to its success and public acceptance. Much of the security risk associated with geological carbon storage stems from its buoyancy. Gaseous and supercritical CO₂ are less dense than formation waters, providing a driving force for it to escape back to the surface. This buoyancy can be eliminated by the dissolution of CO₂ into water prior to, or during its injection into the subsurface. The dissolution makes it possible to inject into fractured rocks and further enhance mineral storage of CO₂ especially if injected into silicate rocks rich in divalent metal cations such as basalts and ultra-mafic rocks. We have demonstrated the dissolution of CO₂ into water during its injection into basalt leading to its geologic solubility storage in less than five minutes and potential geologic mineral storage within few years after injection [1–3]. The storage potential of CO₂ within basaltic rocks is enormous. All the carbon released from burning of all fossil fuel on Earth, 5000 GtC, can theoretically be stored in basaltic rocks [4].

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1. Introduction

“All the carbon in the atmosphere, living creatures and dissolved in the oceans is derived from rocks and will – eventually – end up in rocks, the largest carbon reservoir on Earth” [5]. The carbon moves from one reservoir to another in what is called the carbon cycle [6–7]. Humans have accelerated this cycle by mining and burning fossil fuel since the beginning of the industrial revolution. If nothing is done to stem this acceleration, its peak CO₂ concentration could reach more than 1500 ppmv after about 300 years as shown in Figure 1. Recent estimates suggest that increasing atmospheric CO₂ concentration to just 560 ppmv would raise average global temperature by about 3 °C.

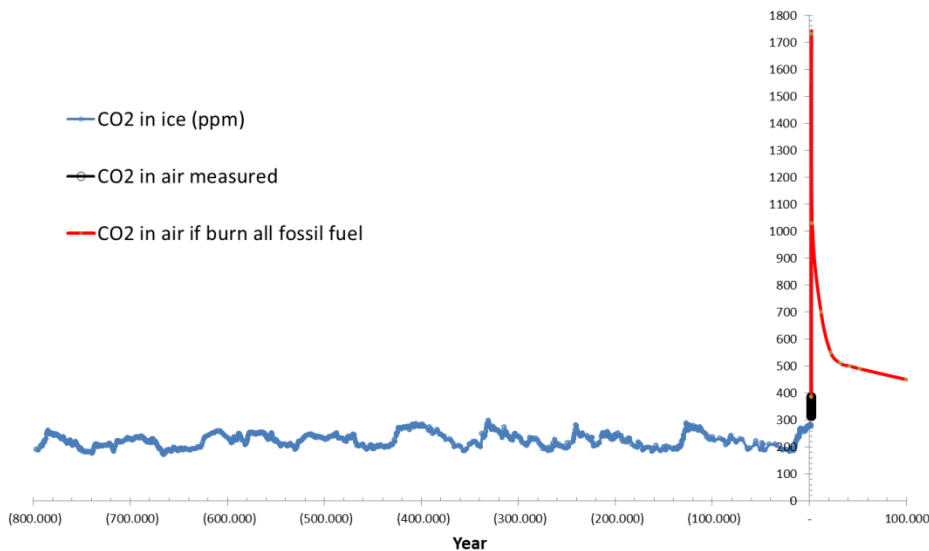


Figure 1. Concentration (ppm) of atmospheric CO₂ during the last 800,000 years [9–14] and 100,000 years into the future if we burn all fossil fuel (5000 GtC) at the current rate increase and do nothing about it [7–8].

Most of the fossil fuel will be finished in 250 years and all in about 500 years [7–8]. If humans burn all fossil fuel at the current rate increase and do nothing to stem the CO₂ emission, it will take the carbon cycle thousands of years to bring the atmospheric concentration below 500 ppm and up to million years to bring the atmospheric concentration to the preindustrial (280 ppm) value.

Human society now has one of three choices: 1) decrease considerably carbon emission, 2) live with the consequences of global warming, or 3) generate the technology to capture CO₂ and safely store it over thousands of years or longer. Much insight into what is the safest long-term storage solution comes from the global carbon cycle. The average time which carbon remains within a particular reservoir is obtained from its residence time. The residence time of carbon in vegetation and soil is on the order of decades, the residence time of carbon dissolved in the deep ocean is on the order centuries, and the residence time of carbon in sedimentary rocks is on the order of millions of years. Carbon within sedimentary rocks is almost exclusively in two forms: carbonate minerals such as calcite and dolomite, and organic carbon, such as fossil fuel, due to organic material burial. By accelerating carbonate mineral formation in subsurface rocks it is possible to rebalance the global carbon cycle, providing a permanent carbon storage solution for thousands to millions of years.

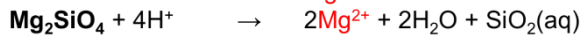
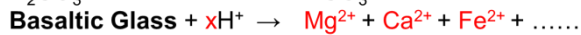
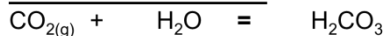
The majority of subsurface carbon storage projects to date have injected supercritical CO₂ into large sedimentary basins. Perhaps the best known of these projects is that at Sleipner, west of Norway, where about one million tonnes of CO₂ has been injected annually since 1996, and stored at more than 700 m below the ocean floor in the Utsira-sandstone. Recent work has shown that the transformation of CO₂ to carbonate minerals in such systems takes at least tens of thousands of years if it occurs at all [15]. This limitation is due to both the slow reactivity of silicate minerals in sedimentary rocks and the lack of the calcium, magnesium, and iron required to make carbonate minerals. An alternative, designed to overcome these limitations, is the injection of CO₂ into reactive basaltic rocks,

rich in these elements, as is currently being explored in southwest Iceland in the CarbFix project [16–17] and the Big Sky Carbon Sequestration Partnership (BSCP) in the northwest United States near Wallula, Washington [18–19].

2. Mineral carbon storage within basaltic rocks. Review of experiments and natural analogues

The injection of carbon dioxide into basaltic rocks has several advantages. First, approximately 25 weight percent of basalt is made of calcium, magnesium, and iron oxides [20–21]. Second, as basaltic rocks are far more reactive in water than sedimentary silicate rocks, the metals contained in basalts are readily available to combine with injected CO₂ to form carbonate minerals [16, 22]. Third, basaltic rocks are highly abundant on the Earth's surface; approximately 8% of the continents [23, 24] and much of the ocean floor is comprised of basalt [25]. These advantages suggest that basalt carbonation could be an important carbon storage solution. The following reactions summarize the dissolution and precipitation reactions (note that the basaltic glass dissolution reaction is not balanced as it is written, several other metals, such as Si, Al etc., are released):

Dissolution reactions:



Forsterite



Diopside



Ca-plagioclase

Precipitation reactions:



siderite, calcite, magnesite, ankerite, ankerite-dolomite.....

Dissolution of CO₂ in water creates carbonic acid. It depends on the partial pressure of CO₂, temperature and salinity how much is dissolved. In pure water at 25 bar pressure and 25°C the total concentration of dissolved inorganic carbon (DIC) is 0,9 mole/kg and the pH is 3.2. The DIC concentration is high, little less than 1/10 of a concentrated HCl acid. It takes considerable amount of rock dissolution reactions, to raise the pH and transform most of that dissolved carbon to bicarbonate (HCO₃⁻). The initial low pH makes the water reactive and the H⁺ ion attacks the basaltic glass and primary minerals containing the divalent cations Ca²⁺, Mg²⁺ and Fe²⁺. The dissolution consumes the H⁺ ion and releases the divalent cations making them available for the carbonate precipitation as described by the last chemical reaction. The abundance of divalent cations will drive the precipitation reaction to the right; but high concentration of H⁺ will hinder the precipitation. However, the dissolution of basaltic glass and primary minerals consumes the H⁺, thus driving the precipitation reaction to the right. It is depended on the relative abundance of the primary minerals and glass, the dissolution rates and thermodynamic stability of the primary minerals and the carbonate minerals, and overall solution composition which carbonate minerals form.

The dissolution rates of the basaltic minerals and glasses are pH dependent. The release of divalent cations will vary with pH at fixed temperature as shown in Figure 2. Pyroxene (Diopside) dissolution rate vary in similar fashion with pH as olivine (Forsterite) but it is slower [28] and Ca-rich plagioclase rate similar to basaltic glass but a bit slower [29]. At pH 3-4, the expected pH in the vicinity of the injection well during injection of CO₂ dissolved in water, dissolution of Mg and Fe containing silica phases, olivine and pyroxene, will dominate, but as pH rises with the dissolution of the primary minerals and glasses, the dissolution of basaltic glass and plagioclase containing Ca becomes faster as the pH rises past 8-9. One would therefore expect Mg-Fe carbonates to dominate at relatively low pH as shown in Figure 3. The Mg-Fe-Ca carbonates at intermedia pH and Ca-carbonates to be most important at the highest pH. This is what is seen in a natural analogue in West Greenland where CO₂ rich fluids invaded basaltic rocks at low temperature [31] and basalt water CO₂ experiments in the laboratory [32, 33]. The carbonates in the altered rocks in West-Greenland are with decreasing partial pressure of CO₂; Fe and Mg rich carbonates; at

intermediate CO₂ pressure Mg-Ca carbonates dominate and at the lowest partial pressure, Ca carbonates are most common.

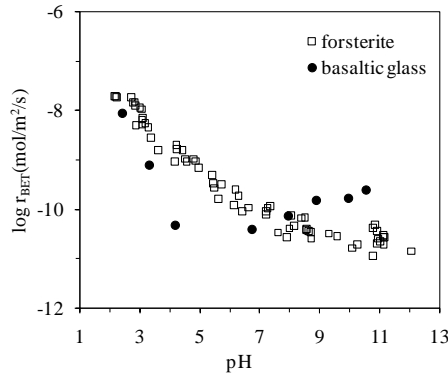


Figure 2. The dissolution rate of the Mg-olivine (Forsterite) at 25°C, [26] and basaltic glass at 30°C, [27] versus pH. The dissolution rate is normalized to the BET-surface area of the dissolving mineral and glass grains.

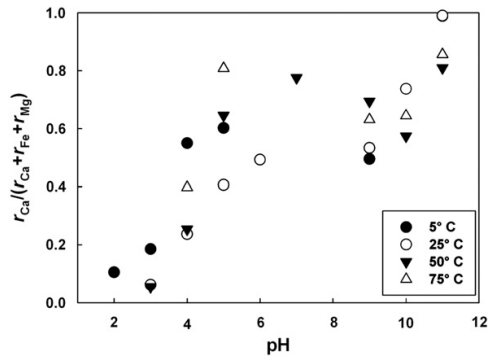


Figure 3. The Ca release rates divided by the sum of the release rates of the major divalent cations from crystalline basalt containing olivine, pyroxene and plagioclase, versus pH at the indicated temperatures [modified from 30].

Dissolution of aluminium silicates rich in divalent cations, releases not only cations that can form carbonates, but also silicon and aluminium that can combine with the divalent cations and precipitate as clays and zeolites. And in turn; diminish the efficiency of basalt carbonation. These secondary minerals compete with the carbonates for the

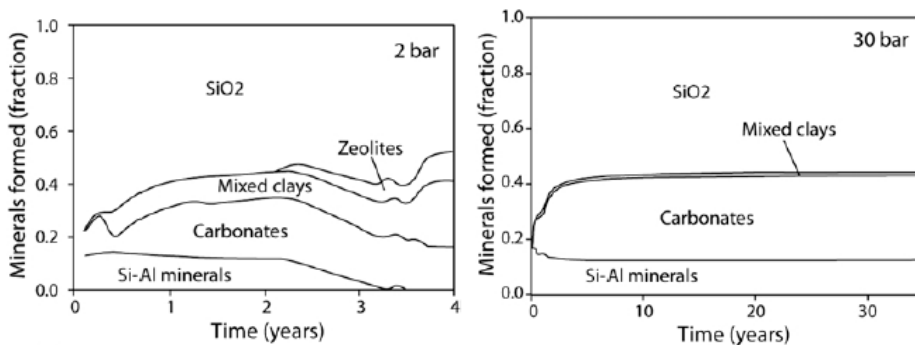


Figure 4. Reaction path batch reactor simulations of basaltic glass dissolution at 25°C (modified from [34]). Carbonate fraction increases relative to clays and zeolites with increasing pCO₂.

divalent cations and the available pore space in the rocks. As can be seen in Figure 4, the higher the partial pressure of the CO₂ the higher the relative fraction of carbonates is formed [34, 35]. It is therefore of advantage to inject at relatively high partial pressure of CO₂; it saves water and pore space. This predicted reaction path simulation has been confirmed by experiments in the laboratory [32, 33].

The question remains; will coating of primary minerals and glasses by secondary minerals such as carbonates and clays halt primary mineral dissolution and therefore the release of divalent cations? As shown in Figure 5 for basaltic glass, modest coating of pyroxene (diopside) and basaltic glass will not stop the dissolution rate [36, 37].

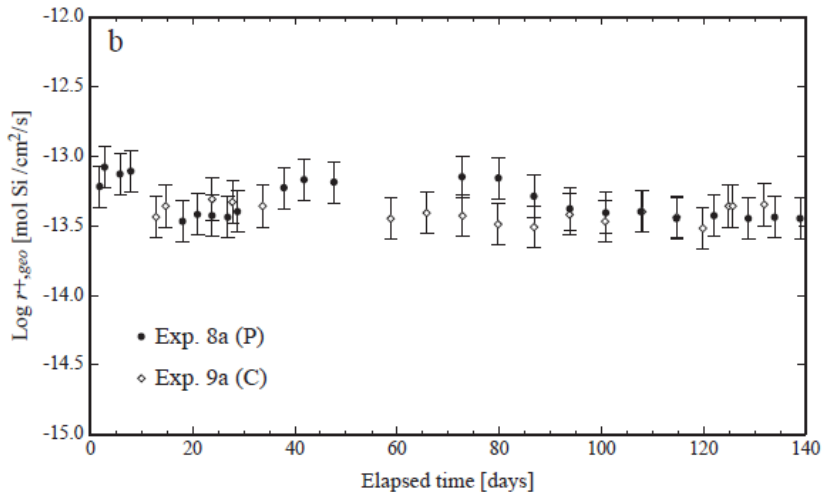


Figure 5. Dissolution rate of basaltic glass with carbonate coatings (P) and dissolution rate of basaltic glass without coatings (C) at pH 10 and 25 °C [modified from 36].

Dissolution of the primary minerals will release several trace metals that can be harmful for life. Metal aquatic concentrations of Al, Cr, Fe and Mn have been shown to surpass standards for the quality of water intended for human consumption at the early stage of basalt-water-CO₂ interactions conducted at high CO₂ pressure in column experiment in the laboratory at low pH; 3–4 [38–40]. However, natural analogue studies from active volcanoes in Iceland have shown that when the pH of the natural water rises up to the neutral range and higher, the metals are in very low concentrations [41–43]. Secondary minerals like ironoxyhydroxides and carbonates will scavenge the released metals and thereby “clean” the water.

3. Field injections: Dissolution of CO₂ in water within the injection well.

One challenge to basaltic rock carbonation is the buoyancy of CO₂. If CO₂ is injected as a separate phase, CO₂ could rise towards the Earth’s surface through pores and fractures eventually escaping back to the atmosphere. This challenge has been overcome at the CarbFix1 pilot injection site in southwest Iceland, where CO₂ was dissolved in water within the injection well as shown in Figure 5 in less than five minutes. In other words, solubility trapping [1]. The CO₂ was dissolved by releasing it as small gas bubbles at 350 m depth into the down-flowing water. Once dissolved, CO₂ is no longer buoyant, and the CO₂ charged water accelerates metal release from basalt and thus mineral trapping as described in chapter 2. The disadvantage of this CarbFix method is that it requires substantial water; only about 5% of the injected mass is CO₂.

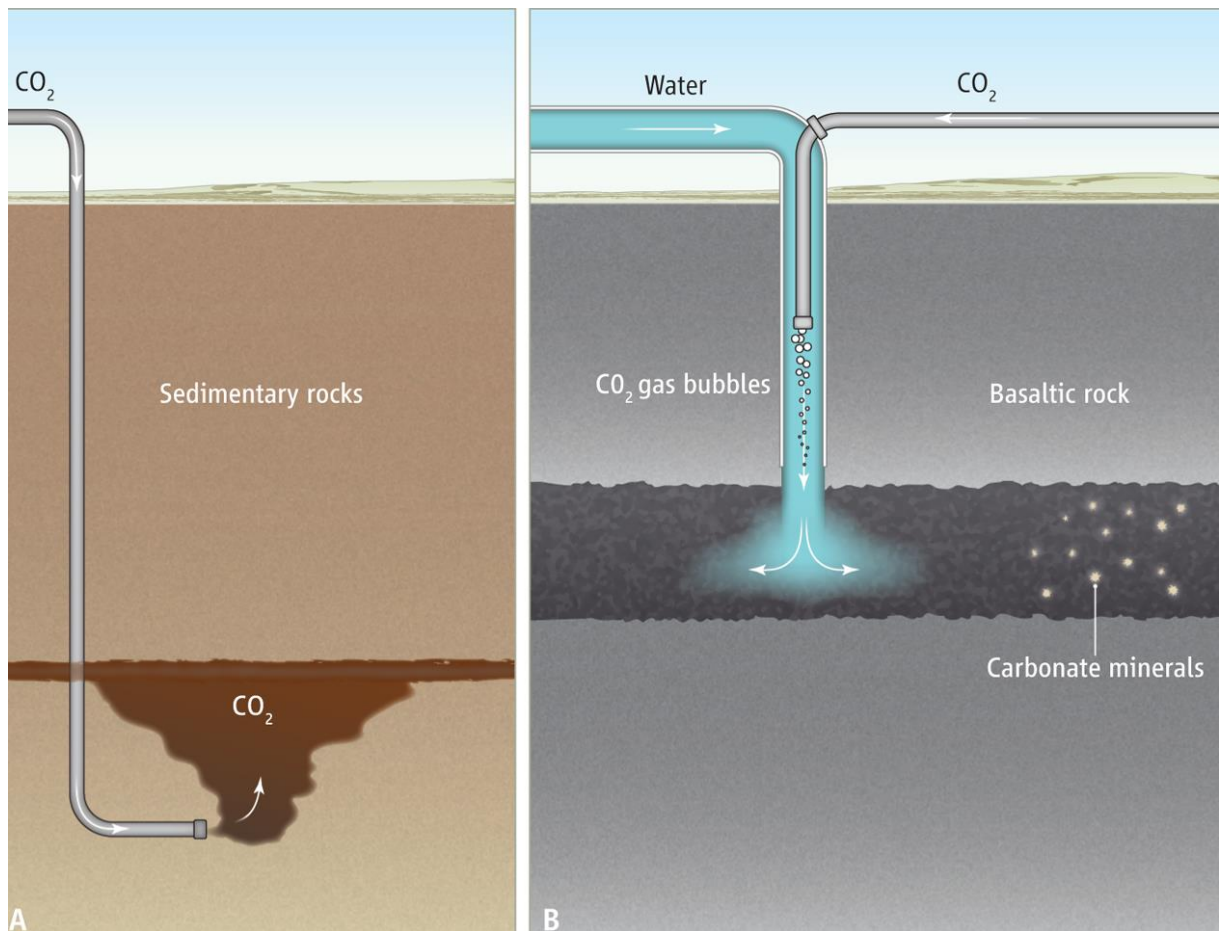


Figure 6. Carbon storage in sedimentary basins and basaltic rocks (from [5]). (A) Carbon storage in sedimentary basins proceeds via the injection of pure CO₂ into porous sedimentary rocks. Ideally this CO₂ is trapped below an impermeable cap rock (structural trapping, [44]). Eventually some of this CO₂ becomes stuck in small pores, limiting its mobility (residual trapping). Over time, CO₂ dissolves in the formation water (solubility trapping). Some of this dissolved CO₂ reacts to form stable carbonate minerals (mineral trapping). As one progresses from structural to mineral trapping, the CO₂ becomes more immobile and thus the storage more secure, though this process can take thousands of years or more[44]. (B) In the CarbFix method, CO₂ is dissolved into water during its injection into porous basaltic rocks. No cap rock is required because the dissolved CO₂ is not buoyant and does not migrate back to the surface. Solubility trapping occurs immediately, and the bulk of the carbon is trapped in minerals within few years [1,2,3,5].

4. Mineral storage within basaltic rocks: Review of pre-injection characterization of the Carbfix 1 injection site in SW-Iceland.

This CarbFix 1 injection site is located adjacent to the Hellisheidi geothermal power plant in SW Iceland, at 260–290 m.a.s.l., 30 km east of Reykjavík (see Fig. 7). The power plant, owned by Reykjavík Energy, currently produces 40,000 tons of CO₂ and 12,000 tons of H₂S per year. These gases are a by-product of geothermal energy production and are of magmatic origin. A 60 tonnes of CO₂–H₂S–H₂ gas mixture, following its separation from other non-water soluble geothermal gases, was transported in a pipeline to the injection site shown in Fig. 7 in 2012. Prior to that a pure CO₂ injection test was performed at this site in 2011 and early 2012, where 175 tons of pure commercial CO₂ was injected [1]. Both the gas and the water were labelled with reactive and non-reactive tracers

and radioactive carbon. The gases were fully dissolved within the injection well as described previously, resulting in a single fluid phase entering the storage formation. This gas charged water is acidic and thus reactive. This injection site has been outfitted with one 2000 m deep injection well, ten monitoring wells ranging from 50 to 1300 m in depth, and various injection and monitoring equipment [1, 2, 3, 16, 17, 21, 45, 46, 47]. The target zone for injection was the lava flow formation at 400-800 m depth and temperature range of 20-50 °C (Fig. 7).

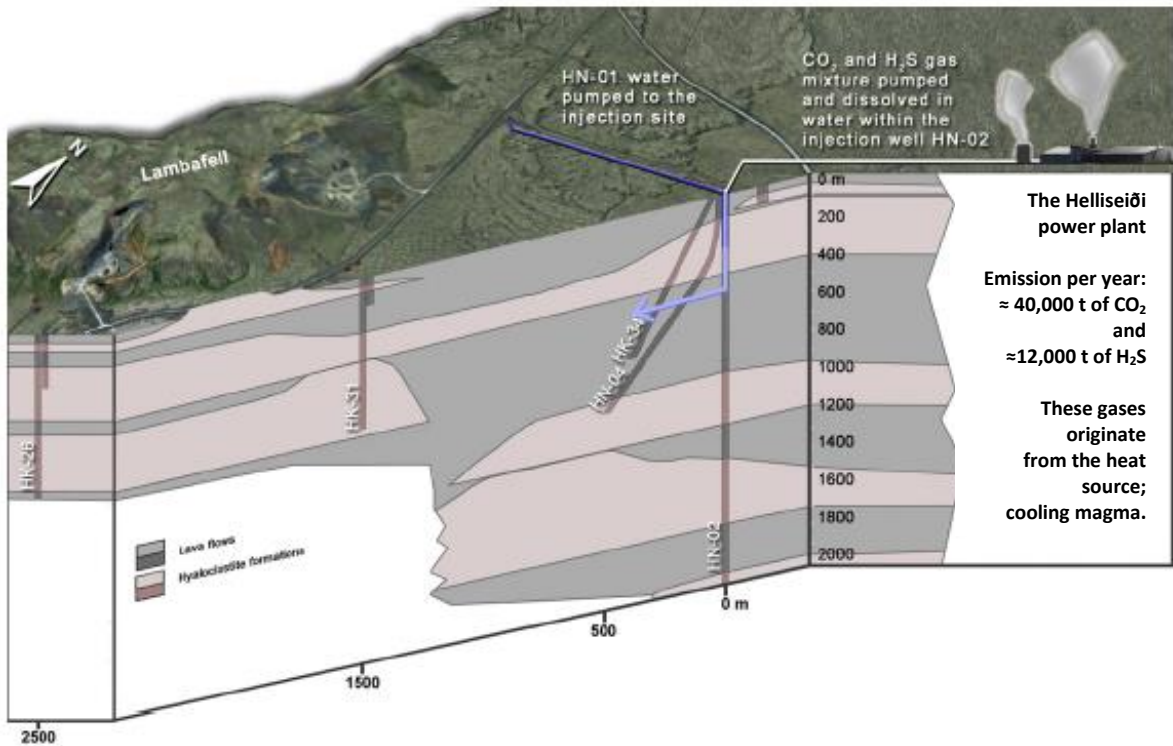


Fig. 7. Geological cross section of the Carbfix 1, injection site. The CO_2 and $\text{CO}_2\text{-H}_2\text{S-H}_2$ gas mixture were pumped toward the injection site and mixed with water from well HN-1 within the injection well HN-2. The gas charged waters enters the basaltic formations as single phase; water phase (modified from [21]).

The pH of the water in the target zone prior the injection was high; 8-10, reflecting the dissolution of the primary basaltic minerals and the ensuing consumption of the H^+ ion as described in chapter 2. The *in situ* partial pressure of CO_2 within the target zone was lower than in the atmosphere; $10^{-3.4}$ bar. Common secondary minerals within the target zone are calcite (Ca-carbonate), Ca-Na-rich zeolites and Mg-Fe rich clays [21] reflecting the low CO_2 pressure at depth (Figs. 3, 4 and 8). All these minerals are supersaturated or saturated with respect to the groundwater they are in contact with in the target zone, but become undersaturated in the CO_2 charged waters during injection into the injection well and the primary basaltic minerals and glass become more undersaturated than before the injection [21]. Reaction path batch reactor simulations of basaltic glass dissolution at 25°C [21] suggests that water rock interactions will over time rise the pH of the reacting solutions resulting in lowering the partial pressure of CO_2 below atmospheric pressure similar to pre-injection condition as shown in Figure 8.

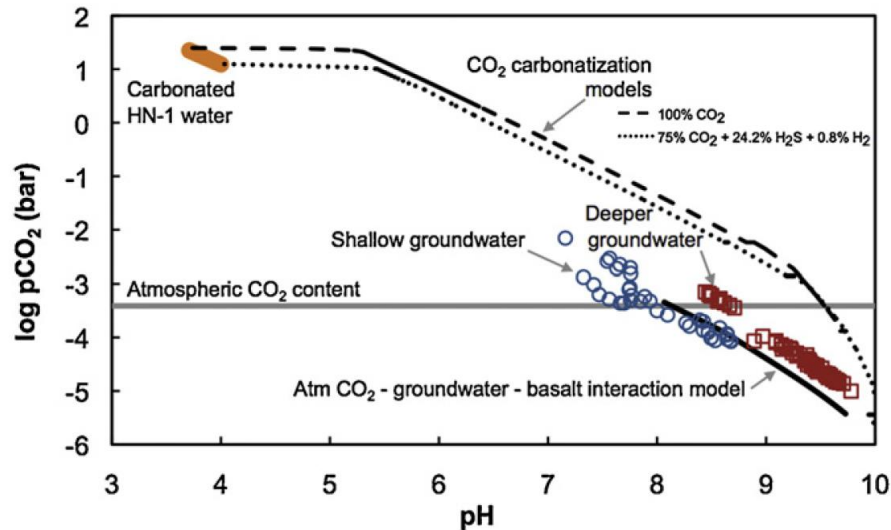


Figure 8. Modelled and measured fluid phase CO_2 partial pressure (in a logarithmic scale) as a function of pH. Blue circles and red squares represent measured water compositions from the shallow and deep wells in Fig. 7 before injection, respectively. The dotted curves show the calculated composition of the gas-charged reaction waters during its interaction with basaltic glass. The grey horizontal line represents the atmospheric pCO_2 . The solid black curve illustrates reaction path modelling of the evolution of atmosphere equilibrated HK-13 water (shallow well) reacted with basaltic glass (modified from [21]).

Reactive transport modelling, where kinetic (dissolution and precipitation rate) and thermodynamic data bases are combined with hydrologic model (TOUGHREACT), was used to predict water rock interactions as the fluid flows through the basaltic rocks at the CarbFix1 injection site (Fig. 9). The results suggested about 80% of the injected CO_2 would be mineralized five years after injection [17, 44]. If this were true, it would change the timescale of mineral trapping of CO_2 considerably [5, 44].

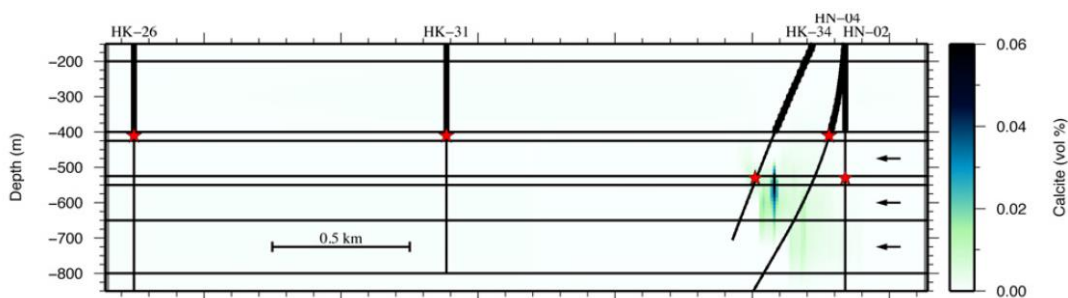


Figure 9. Cross section of the CarbFix injection site showing the location of the injection well HN-2 and some of the monitoring wells and the predicted volume percent of calcite (Ca-carbonate) within the basalts five years after a pure CO_2 injection [modified from 17].

5. Mineral storage within basaltic rocks: Injection of pure CO_2 and H_2S - CO_2 gas mixtures at the CarbFix injection sites in SW-Iceland.

Field injections at the carbfix sites have been performed from 2008 to the present. Tracer test were conducted under natural and forced conditions at the CarbFix1 site from 2008 to 2011, to define the hydrology of the system and scale reactive transport models [47, 16, 45, 17, 46, 2]. Pure CO_2 injection was done in 2011 and 2012. A gas

mixture of CO₂-H₂S-H₂, captured from the power plant, was injected in 2012. By mid-year 2014, CO₂-H₂S gas mixture, captured and separated from the gas stream of the Hellisheidi power plant, has been injected deep into the geothermal system at the CarbFix 2 site. The gas mixture was injected into the geothermal system to lower the capture and gas separation cost and conduct the injection under sterile (free of bacteria) conditions [48].

Hundred and seventy five tonnes of pure CO₂ were injected in 2011 and 2012 to test the injection system and the rate of solubility and mineral storage at 400-800 m depth and 20°-50°C (Figs. 6, 7 and 9). As described in chapter 3, solubility trapping took less than five minutes within the injection well. Most of the injected CO₂ was carbonated within two years at 20-50°C and 500-800 m depth [1, 2, 3].

Seventy three tonnes of CO₂-H₂S-H₂ gas mixture (75%-24%-1%) were injected in the summer of 2012 to test the rate of solubility and mineral storage at 400-800 m depth and 20°-50°C. The conditions were the same as in the previous pure CO₂ injection. Solubility trapping took less than five minutes within the injection well. However the sulphur reactions were fast and some of the sulphur mineralized within the injection well under non-continuous injection when only water was injected, resulting in pH excursion from low pH 3.8 to high pH ; 9-10. Furthermore there was a strong bacteria response to the injection, resulting in loss of injection well transmissivity [48, 49]. Most of the injected CO₂ and H₂S were mineralized within two years at 20-50°C and 500-800 m depth [2, 3].

By mid-year 2014, CO₂-H₂S gas mixture, was captured and separated from the gas stream of the Hellisheidi power plant, dissolved in water at the surface at about 5 bar pressure and 20°C and injected down to the sterile part of the system at 700 m depth and 200 - 270°C . By early September 1,500 tonnes of the gases were injected at this Carbfix2 injection site. CarbFix2 and Reykjavik Energy are aiming at injecting 8,000 - 10,000 tonnes of the gas mixture per year during this experiment [48].

6. The cost of capture and storage.

The CarbFix method requires substantial water. The water needed at 25°C to dissolve 1 kg of CO₂ decreases from 665 kg to 10 kg of H₂O by rising pressure from 1 to 64 bars [16]. There are several possible sources for this water. Porous basalts near the continental margins have huge storage capacities adjacent to nearly unlimited supplies of seawater [16, 25, 50]. On the continents, water can be pumped from the targeted basaltic rock. The injection of CO₂ charged water, however, increases substantially the energy necessary for injection. The energy penalty of the CarbFix method depends on the type and efficiency of the power plant. For the Hellisheidi geothermal power plant in southwest Iceland which emits 21.6 g of CO₂ per kWh of electricity produced, the energy penalty is on the order of 0.2%. For typical coal and gas fired power plants, which emit from 385 to 1000 g of CO₂ per kWh electricity produced [1], the energy penalty will range from 3 to 10%.

A major challenge to all carbon capture and storage projects is the cost. The estimated cost of storing and transporting a tonne of CO₂ at maximum reservoir exploitation at the CarbFix1 site via dissolved water injection is about \$17 [51]; this cost is more than twice that of geologic storage via direct CO₂ injection in typical sedimentary basins [52], but offers enhanced security because CO₂ dissolved in water and stored in minerals is not buoyant (Figs. 6 and 10). Some of the additional cost using the CarbFix method will be paid back during the monitoring period after injection. The storage site has to be safe for at least 1000 years (Figs. 1 and 10) and the storage site will be monitored for that period. Mineral storage sites will need less monitoring than conventional storage of buoyant supercritical CO₂ in sedimentary rocks. However, the cost of carbon capture and storage is still dominated by capture and gas separation, which costs \$55 to \$112/tonne CO₂ as shown in Figure 10 [52]. This capture cost could be lowered by injecting gas mixtures into rocks rather than pure CO₂ as is now being tested at the CarbFix2 site in SW-Iceland.

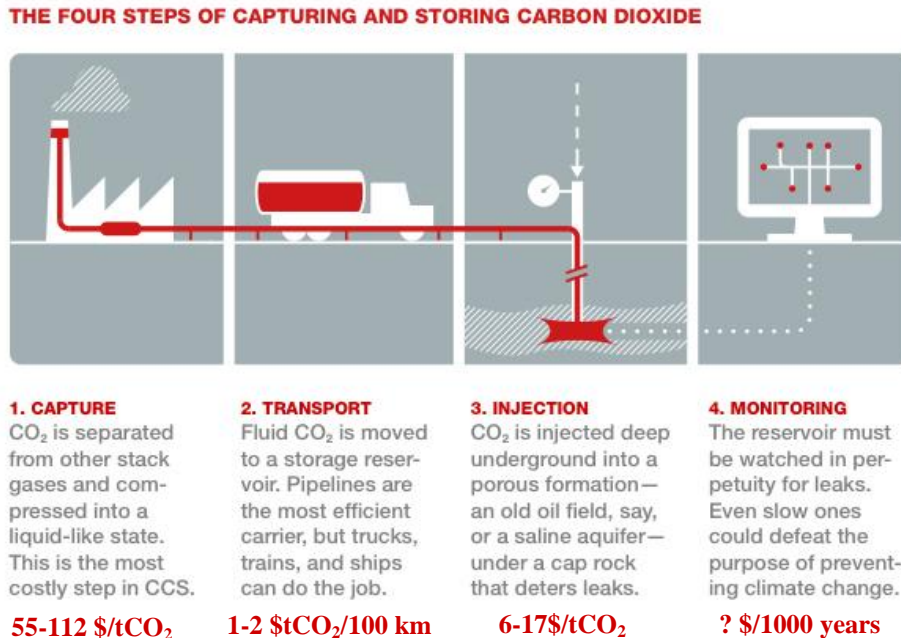


Figure 10. A simplified description of the steps involved in the carbon capture and storage (CCS) process and the cost of each step. The figure is modified from [53]. The cost shown for each step is from references [51, 52].

7. The global CO₂ storage potential in basalt.

If the CarbFix method can be replicated worldwide, it can change the timescale of mineral carbon trapping considerably. Instead of taking thousands of years, mineral trapping via basalt carbonation can be complete within years. Once completed, the risk of leakage is reduced and one can walk away from the storage site with minimal further monitoring.

Basaltic rock injection is still in its infancy, though if it can be up scaled, it may provide a safe alternative to the injection of pure CO₂ into sedimentary basins. Natural analogues in Iceland, the largest landmass of the oceanic ridges above sea level, have shown that up to 70 kg CO₂ can be stored in a cubic metre of basaltic rock [54]. If these natural analogues in Iceland are used to upscale to the storage potential of all the ocean ridges, we get a huge number [4]. The storage potential of the oceanic ridges is orders of magnitude larger than the estimated CO₂ emission; 5000 GtC, stemming from burning of all fossil fuel on Earth[7] shown in Figure 1. The question remains; how much of this storage potential will be of practical use in the future [5].

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