Radiocarbon as a Reactive Tracer for Tracking Permanent CO_2 Storage in Basaltic Rocks

Type of Report: Final Scientific/Technical

Reporting Period Start Date: October 1, 2010

Reporting Period End Date: September 30, 2015

Principal Author(s):

Juerg M. Matter, PI, Columbia University, Lamont-Doherty Earth Observatory

Martin Stute, Lamont-Doherty Earth Observatory

Peter Schlosser, Columbia University

Wallace Broecker, Columbia University

Report Issue Date 12/31/2015

DOE Award Number: DE-FE0004847

Submitting Organization: The Earth Institute / Lamont-Doherty Earth Observatory

Columbia University
61 Route 9W
Palisades, NY 10964

Submitted to:

U.S. Department of Energy
National Energy Technology Laboratory

DOE Project Manager: Karen Kluger

DISCLAIMER

ABSTRACT

In view of concerns about the long-term integrity and containment of CO_2 storage in geologic reservoirs, many efforts have been made to improve the monitoring, verification and accounting methods for geologically stored CO_2. Our project aimed to demonstrate that carbon-14 (^{14}C) could be used as a reactive tracer to monitor geochemical reactions and evaluate the extent of mineral trapping of CO_2 in basaltic rocks. The capacity of a storage reservoir for mineral trapping of CO_2 is largely a function of host rock composition. Mineral carbonation involves combining CO_2 with divalent cations including Ca^{2+}, Mg^{2+} and Fe^{2+}. The most abundant geological sources for these cations are basaltic rocks. Based on initial storage capacity estimates, we know that basalts have the necessary capacity to store million to billion tons of CO_2 via in situ mineral carbonation. However, little is known about CO_2-fluid-rock reactions occurring in a basaltic storage reservoir during and post-CO_2 injection. None of the common monitoring and verification techniques have been able to provide a surveying tool for mineral trapping. The most direct method for quantitative monitoring and accounting involves the tagging of the injected CO_2 with ^{14}C because ^{14}C is not present in deep geologic reservoirs prior to injection. Accordingly, we conducted two CO_2 injection tests at the CarbFix pilot injection site in Iceland to study the feasibility of ^{14}C as a reactive tracer for monitoring CO_2-fluid-rock reactions and CO_2 mineralization. Our newly developed monitoring techniques, using ^{14}C as a reactive tracer, have been successfully demonstrated. For the first time, permanent and safe disposal of CO_2 as environmentally benign carbonate minerals in basaltic rocks could be shown. Over 95% of the injected CO_2 at the CarbFix pilot injection site was mineralized to carbonate minerals in less than two years after injection. Our monitoring results confirm that CO_2 mineralization in basaltic rocks is far faster than previously postulated.

KEYWORDS

Monitoring, verification and accounting, CO_2 mineralization, CarbFix, radiocarbon, sulfurhexafluoride, trifluoromethyl sulfur pentafluoride

TABLE OF CONTENTS

EXECUTIVE SUMMARY

In October 2010, the Earth Institute at Columbia University in the City of New York began work on a U.S. Department of Energy (DOE) funded project titled, *Radiocarbon as a Reactive Tracer for Tracking Permanent CO_2 Storage in Basaltic Rocks*. The main objective of the project was to demonstrate that carbon-14 (^{14}C) could be used as a reactive tracer to monitor geochemical reactions in CO_2 injection reservoirs and to evaluate the extent of mineral trapping. Carbon-14 is naturally produced in the atmosphere. Its half-life is of 5730 years and it is produced from cosmic rays interacting with nitrogen in the air. Due to its relatively short half-life, it is essentially non-existent in the deep sub-surface where CO_2 would be stored. CO_2 produced from the combustion of fossil fuels also does not contain any ^{14}C and thus would be perfectly camouflaged among pre-existing CO_2 or carbon in the geologic subsurface. In order to identify and monitor it in the subsurface, the goal was to label the injected CO_2 with ^{14}C that makes it look like normal surface carbon or atmospheric CO_2.

None of the currently suggested approaches to monitor and verify CO_2 storage in geologic reservoirs are able to provide a surveying tool for dissolved CO_2 and mineral trapping. The most direct methods involves the tagging of the injected CO_2 with ^{14}C because ^{14}C is not present in deep reservoirs prior to injection and is detectable in small quantities. The focus of the work discussed in this report is on the conduction of two CO_2 injection experiments at the CarbFix pilot injection

site in Iceland and on the application of non-reactive and reactive tracers to evaluate *in-situ* CO_2 mineralization in basaltic rocks for permanent and safe storage of CO_2.

The CarbFix pilot project in Iceland was designed to promote and verify permanent CO_2 storage in basaltic rocks via *in-situ* mineralization (www.carbfix.com). Two injection tests were performed: Phase I test involved the injection of 200 tons of CO_2, and Phase II a 73 tons injection of a CO_2+H_2S gas mixture. The injection site is located about 25 km east of Reykjavik and is equipped with one (2000 m deep) injection well (HN02) and 8 monitoring wells ranging in depth from 150 to 1300 m. The target CO_2 storage formation is between 400 and 800 m depth and consists of basaltic lavas. The injected gases were injected fully dissolved in water due to the shallow depth of the target storage reservoir. Non-reactive (SF_6, SF_5CF_3) and reactive (^{14}C) tracers were used to monitor CO_2 transport and reactivity in the reservoir. SF^6 and SF_5CF_3 tracers were continuously injected into the gas stream (CO_2, H_2S), whereas a ^{14}C-labelled solution was continuously injected into the water stream. For the Phase I and II injections, the ^{14}C concentrations of the injected solutions were 40.0 Bq/L and 6 Bq/L, respectively. The ^{14}C concentration of the dissolved inorganic carbon (DIC) in the storage reservoir prior to injections was 0.0006 Bq/L.

Fluid samples for SF_6, SF_5CF_3, ^{14}C, DIC and pH analyses were collected without degassing in the injection and monitoring wells using a specially designed downhole sampler or a submersible pump from 2010 to date for the purpose of monitoring the fate of the CO_2 in the storage reservoir. The tracer breakthrough curves of SF_6 and SF_5CF_3 from the first monitoring well (HN04), which is 70 m downstream from the injection well at 400 m depth, reveal a double peak, with the first tracer/injectate arrival around 56 days after injection started. This was followed by slightly decreasing tracer concentrations before further concentration increase occurred, with peak concentrations around 400 days after injection. The double peak tracer breakthrough curves are in agreement with the hydrogeological model of the test site, showing a relatively homogenous porous storage formation intersected by a low volume and fast flow path that channels about 3% of the tracer flow between HN02 and HN04.

The DIC, pH and ^{14}C concentration time series data in HN04 were initially coincident with the SF_6 and SF_5CF_3 data series showing peak concentration or lowest pH values around 56 days after injection. Subsequently, ^{14}C and DIC concentrations decreased and stayed constant for the rest of the remaining monitoring period. Mass balance calculations of DIC and ^{14}C, corrected for any mixing between the injectate and the ambient groundwater, show that between 95 and 98% of the injected CO_2 has been mineralized through CO_2-fluid-rock reactions between the injection and the monitoring wells between 2012 and 2015. Mineralization of the injected CO_2 was confirmed by retrieving a rock core from the injection reservoir and mineral material from monitoring well HN04. SEM-EDXS analysis on the collected mineral material reveals calcite as the dominant mineral phase. Carbon-14 analysis of the calcite show elevated ^{14}C values, similar to values analyzed for the DIC of the groundwater in the monitoring well.

Tracer results of this work demonstrate for the first time nearly complete CO_2 mineralization in basaltic rocks within less than two years. The newly developed tracer techniques, using non-reactive and reactive tracers, allowed for quantitative monitoring of dissolved and mineralized CO_2 that is not possible with conventional monitoring technologies.

REPORT DETAILS

Introduction

The permanence and long-term safety of geological CO_2 storage is key for a successful deployment of carbon capture and storage (CCS) on a large scale. Conventionally, CO_2 is injected as dry CO_2 into reservoirs at depths below 800 m where CO_2 is in a supercritical state (Metz et al., 2005). At this depth, the injected CO_2 is stored as a buoyant fluid in contact with reservoir brines and rocks, and cap rock formations. The buoyancy of supercritical CO_2 requires high integrity of the cap rocks, which may degrade over time as a function of CO_2-fluid-rock reactions. Thus, the permanence and long-term safety of geological CO_2 storage is determined by *in-situ* CO_2-fluid-rock reactions. Injection of CO_2 modifies ambient formation waters, inducing fluid-rock reactions that may result in the immobilization of the injected CO_2 (IPCC, 2005), or alternatively to increased permeability.

Once injected, various trapping mechanisms result in the immobilization of the injected CO_2. Besides physical trapping below a low permeability cap rock, or trapping as a residual phase or dissolved in ambient brines, reaction of CO_2 with reservoir rocks to form solid carbonate minerals provides permanent and safe storage (e.g. Bachu et al., 1994). The capacity of a storage reservoir for CO_2 mineralization to carbonate minerals is largely a function of host rock composition. Basalt and ultramafic rocks such as mantle peridotite, both rich in Ca, Mg, Fe silicate minerals, have a high reactivity with CO_2, enabling the mineralization of CO_2 to stable carbonate minerals such as calcite, magnesite, dolomite and siderite (e.g. Goldberg et al., 2008; Matter and Kelemen, 2009; Schaef et al., 2010).

The research, summarized in this report, provides the groundwork of accelerated permanent CO_2 storage in unconventional storage reservoirs such as basalt as well as of a new monitoring and verification technology. The storage approach involves the injection of CO_2 dissolved in water into basalt, whereas the newly developed monitoring technology involves the combination of non-reactive and reactive tracers for quantitative monitoring and verification of geologically stored CO_2. The novel injection technology developed by the CarbFix team allows for continuous co-injection of water and CO_2 gas into an injection well (Figure 1). The injected water could be wastewater from a power plant or groundwater from the target storage reservoir that was pumped to the surface and re-injected in the CO_2 injection well. Typical injection rates during the Phase I injection were 70 g/s for CO_2 and 1800 g/s for H_2O, respectively. The advantage of dissolving CO_2 into H_2O during its injection is that buoyancy is not an issue anymore as soon as the CO_2 gas is fully dissolved in H_2O thereby increasing the storage security by avoiding the need to rely on structural or stratigraphic trapping mechanisms (Sigfusson et al., 2015). Furthermore, CO_2-charged water accelerates the release of base cations such as Ca, Mg and Fe from the basalt and thus the CO_2 mineralization in form of solid carbonate minerals.

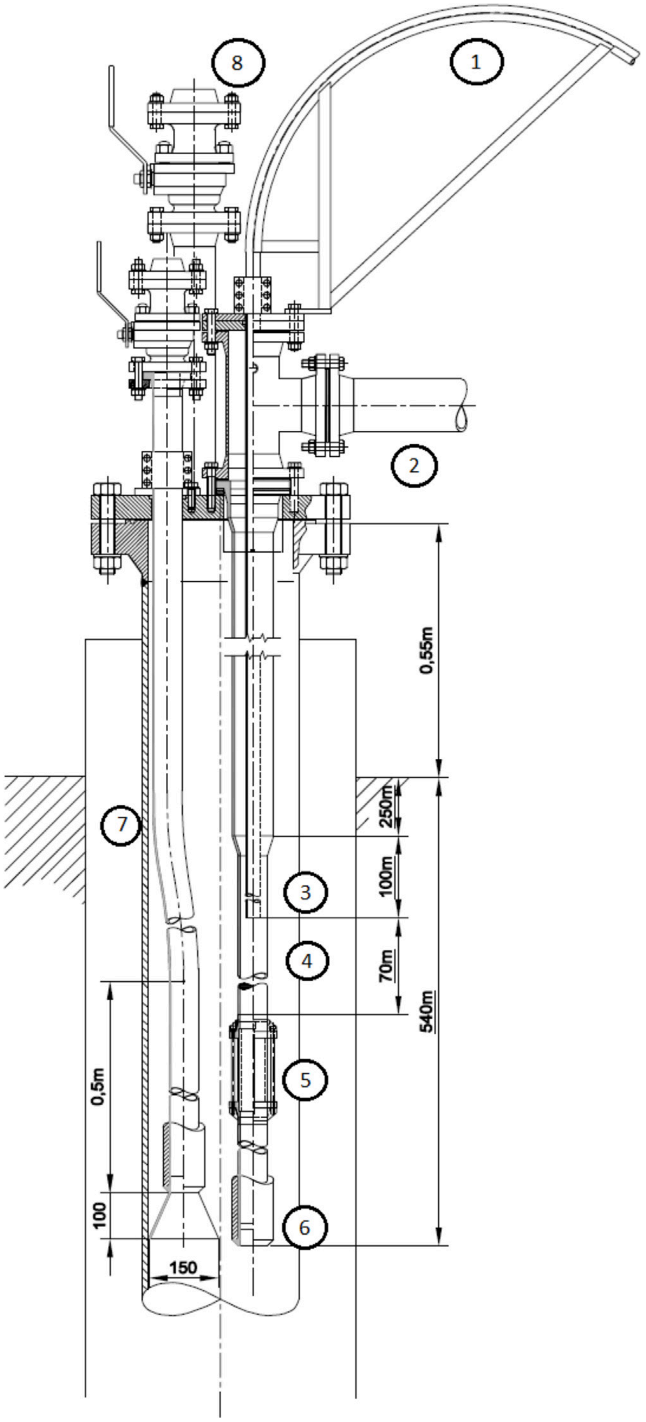

Figure 1. CarbFix CO_2 injection system. (1) CO_2 injection pipe, (2) water injection pipe, (3) CO_2 sparger, (4) outer mixing pipe, (5) mixer, (6) fluid outlet, (7) service pipe for downhole sampling. and observations, (8) service entry to well head space. From Sigusson et al. 2015.

Monitoring/Verification/Accounting (MVA) technologies are key to proof to the authorities and to the public that carbon capture and storage is safe. Geophysical methods such as 4D seismic, crosswell seismic, VSP and wireline logging, are powerful tools to track the migration of CO_2 within a storage reservoir and for providing information about the location and concentration of CO_2 within the reservoir (e.g. Benson et al. 2004, Metz et al., 2005, Hovorka at al. 2006, Hoversten et al. 2006). However, most of these detection methods require CO_2 to be present as a supercritical phase. Dissolved CO_2 and chemically transformed carbon thus avoid detection. Carbon in form of dissolved inorganic carbon or carbonate minerals resident in the formation prior to injection further impedes monitoring. We therefore developed and tested the feasibility of a new monitoring technology that involves the tagging of CO_2 that is injected with ^{14}C. Carbon-14 and carbon-13 as tracers in geological CO_2 storage are of special interest (Bachelor et al. 2008, Lackner and Brennan, 2009). Carbon-13 has been successfully used to trace the movement of CO_2 in a storage reservoir, and to characterize geochemical reactions that were induced as a result of a CO_2 injection (Mayer et al. 2013). It is quite clear that there is no better tracer than carbon itself to monitor the fate of the injected CO_2 in the subsurface. Carbon has two stable, nonradioactive isotopes, ^{12}C and ^{13}C and one radioactive isotope, ^{14}C. The ratio of $^{13}C/^{12}C$ is 0.01, whereas the ratio of $^{14}C/^{12}C$ in the modern atmosphere is $1.3x10^{-12}$. ^{14}C decays with a half-life of 5730 years. ^{14}C activities or concentrations are generally reported as “percent modern carbon” (pmc), which is defined as 95% of the ^{14}C activity of an NBS oxalic acid standard in

1950. Due to long residence times, carbon in deep geologic reservoirs typically contains less than 0.5 pmc of ^{14}C, making ^{14}C an ideal tracer for injected CO_2. During carbonate precipitation processes, the solid phase will be enriched in the heavier isotopes (^{13}C and ^{14}C) and the remaining dissolved CO_2 will become isotopically lighter (Clark and Fritz, 1997). During this process, ^{14}C is only minimally affected by isotope fractionation relative to its precision of measurement. Natural carbon in the CarbFix CO_2 storage reservoir is low in ^{14}C and the precipitated tagged carbon should be easily identifiable in solid samples from the aquifer.

Overall, the tagging with ^{14}C in combination with non-reactive tracers (SF_6, SF_5CF_3), and sample collection allows detection of dissolved and chemically transformed CO_2 and thus adds an important additional monitoring and verification technique to our toolbox.

The goal of the described project was to study the feasibility of permanent CO_2 mineralization in a basaltic storage reservoir and to test the ^{14}C tagging method as a quantitative monitoring and verification tool for carbon capture and storage on a field scale. This was implemented at the CarbFix pilot injection site in SE Iceland. The CarbFix pilot project was designed to promote and verify in-situ mineralization of CO_2 in basaltic rocks. The pilot injection site is situated about 25 km east of Reykjavik and is equipped with one 2000 m deep injection well (HN02) and eight monitoring wells ranging in depth from 150 to 1300 m (Figure

2). The target CO_2 storage formation was between 400 and 800 m depth, consisting of basaltic lava flows with lateral and vertical permeabilities of 300 and 1700 x 10-15 m^2, respectively (Aradottir et al. 2012). Two injection tests were performed in 2012: Phase I included a 200 ton of pure CO_2 injection, and Phase II a 73 ton injection of CO_2+H_2S of which 55 tons were CO_2. In both tests, the gases were injected fully dissolved in water using the above-mentioned novel CO_2 injection system because the storage reservoir was too shallow for a supercritical CO_2 injection. Nonreactive (SF_6, SF_5CF_3) and reactive (^{14}C) tracers were continuously co-injected with the CO_2. Fluid samples were regularly collected in the monitoring wells for tracer analysis. Concerning the mixed gas injection, we had to stop the injection because of decreasing injectivity in the injection borehole. Injectivity could be recovered by high pressure airlift testing, however analysis of fluid and particulate samples collected during the well recovery test indicated that biofilms and to a minor extent precipitation of iron-oxyhydroxides were the cause of the clogging of the pore space in the injection borehole. The growth of biofilms and the precipitation of secondary iron-oxyhydroxides were most likely induced by small amounts of dissolved oxygen in the system. Thus, we concluded that we could not continue with the mixed gas injection in this shallow reservoir because of the issue of clogging of the injection borehole with biofilms.

The common view in the scientific community has been that mineral trapping will take hundred to thousand of years (IPCC, 2005). Thus, the safety and security of geologic CO_2 storage will rely on the integrity of cap rocks as well as on physical trapping processes. This project aimed to proof the feasibility of CO_2 mineralization in a basalt storage reservoir. The conducted injection tests are truly on a pilot scale and thus are only the first step in a much larger effort. Now that fast CO_2 mineralization for permanent CO_2 storage in basalt has been developed, upscaling to much larger injection volumes should be seriously considered.

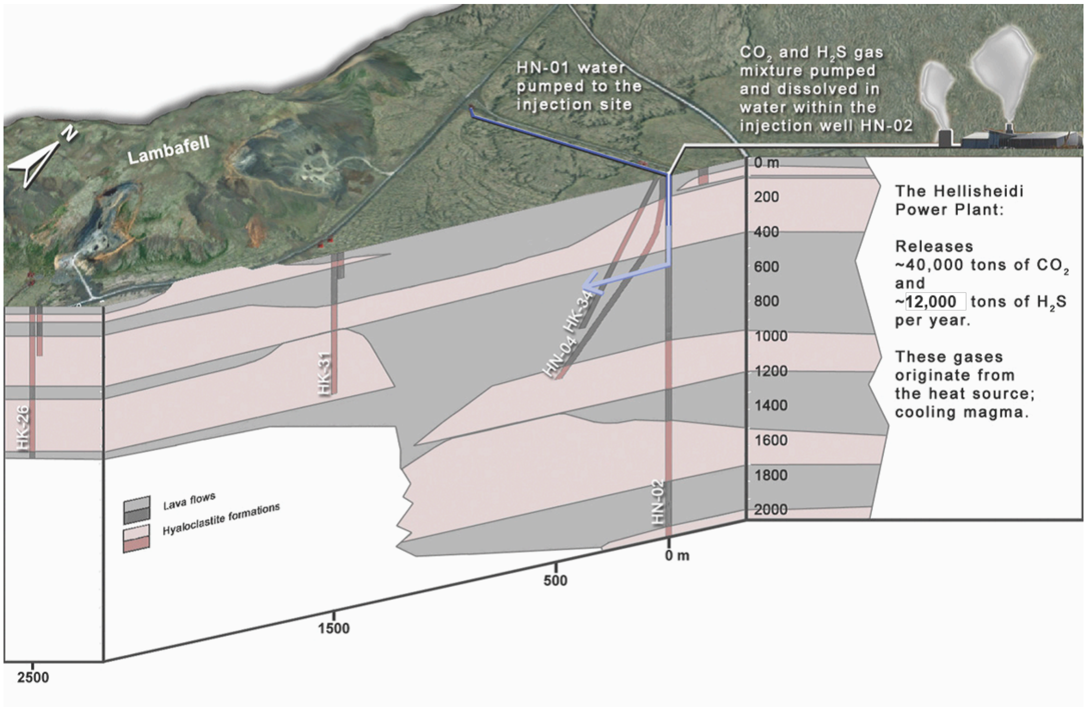

Figure 2. Geological cross-section of CarbFix injection site. CO_2 and H_2S were injected fully dissolved in water in the injection borehole HN02. Fluid samples were collected in observation boreholes downstream from the injection borehole for monitoring and verification of the dissolved gas injection (modified from Alfredsson et al., 2013).

Summary of Tasks

The goal of the project was to demonstrate that carbon-14 (^{14}C) can be used as a reactive tracer to monitor geochemical reactions in an injection reservoir and to evaluate the extent of mineral trapping in basaltic rocks. The project objectives were to test ^{14}C as a reactive tracer for geochemical reactions caused by CO_2 injection and to quantify the extent of in-situ mineral carbonation in a basaltic storage reservoir. Beyond the management task, the project was structured in four major technical tasks to accomplish the overall goal and project objectives:

- Task 2.0 Monitoring the CO_2 movement with SF_6 and SF_5CF_3 in the basalt formation.
- Task 3.0 Monitoring of geochemical reactions and in-situ mineral carbonation with ^{14}C.
- Task 4.0 Mineral carbonation studies on core samples
- Task 5.0 Quantification of mineral carbonation in the CarbFix basalt storage reservoir.

The basic research steps of the project were organized into the set of tasks listed above. The remainder of the report describes each of the four technical tasks activities and results. A Conclusion section follows this.

Task 2.0 Monitoring the CO_2 movement with SF_6 and SF_5CF_3 in the basalt formation

The objective of this task was to use SF_6 (sulfur hexafluoride) and SF_5CF_3 (trifluoromethyl sulfur pentafluoride) as non-reactive tracers to monitor the transport of the injected CO_2-saturated solution in the storage reservoir.

Experimental Methods

SF_6 was used for Phase I (pure CO_2) and SF_5CF_3 for Phase II injection (CO_2 + H_2S), respectively. The tracer injection system consisted of two gas cylinders, each containing SF_6 or SF_5CF_3 (Figure 3).

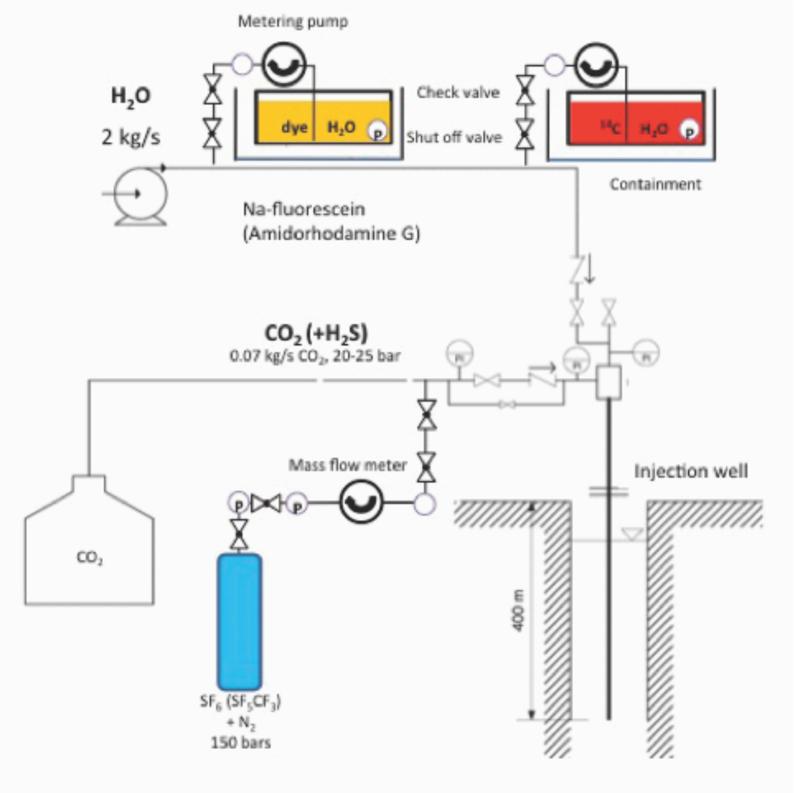

Figure 3. Non-reactive and reactive tracer injection system. SF_6 and SF_5CF_3 were injected from gas cylinders using a mass flow meter.

These non-reactive gases were mixed into the CO_2 and CO_2+H_2S gas stream using mass flow meters. The ratio of CO_2 and SF_6 or CO_2 and SF_5CF_3 in the injection well were carefully monitored by collecting fluid samples in the injection well using a specific bailer system that allows retrieving fluid samples at in-situ pressure conditions. Tracer concentrations in the injected solution are listed in Table 1.

Furthermore, fluid samples were collected in the monitoring wells using submersible pumps that were permanently installed in the monitoring wells. Fluid samples for SF_6 and SF_5CF_3 analyses were collected in evacuated 100 ml glass serum bottles by technicians of Reykjavik Energy. Sample bottles were shipped to our laboratory for analysis on a regular schedule. Concentrations in the headspace were measured with a precision of ±2% using gas chromatography (SRI 8610C) and ultrapure nitrogen as the carrier gas.

Table 1. Injection test parameters from Phase I and II injections.

Injection Phase	CO_2 (tons)	H_2O (liters)	SF_6 (ccSTP/cc)	SF_5CF_3 (ccSTP/cc)	^{14}C (fraction modern)	DIC (mol/L)	pH
I	200	4.8×10^{6}	2.33×10^{-8}	none	16.17	0.82	3.85 (@20°C)
II	54.75	2.25×10^{6}	none	2.24×10^{-8}	4.65	0.43	4.03 (@20°C)

The headspace samples were injected into a 6ft long, 1/8” wide pre-column with a 5 ångström molecular sieve (MS-5A) and a 6ft chromatographic column at

60°C. SF_6 and SF_5CF_3 concentrations were measured using a SRI 8610C gas chromatograph with an electron capture detector and a Alltech Carbograph column. Results were recorded using the PeakSimple 3.07.2 software, and concentrations in the water samples were calculated based on the volume of headspace and the solubility.

Results and discussion

SF_6 and SF_5CF_3 are two non-reactive tracers that were used to assess plume migration from the injection well to the monitoring wells in the storage reservoir. The SF_6 and SF_5CF_3 concentrations in the injected CO_2-saturated solution were 2.33×10^{-8} ccSTP/cc and 2.24×10^{-8} ccSTP/cc, respectively (Table 1). An increase of SF_6 and SF_5CF_3 concentrations in fluid samples retrieved from the first monitoring well (HN04) confirm the arrival of the CO_2-saturated solution in the monitoring well. Based on the SF_6 data, the initial breakthrough of the CO_2 saturated solution from Phase I injection occurred 56 days after injection (Figure 4). Subsequently, the SF_6 concentration decreased before a further increase in concentration occurred, with peak concentration measured 406 days after initiation of the injection, followed by a constant trend of decreasing SF_6 concentration until the end of the monitoring period (Figure 4). Gaps in the SF_6 data record between 500 and 650 days are due to a failure of the submersible pump in borehole HN04. The pump broke down and had to be replaced by a new one twice. SF_5CF_3, used during the Phase II injection, behaved similarly. Its initial arrival in monitoring well HN04 occurred 58 days after initiation of Phase II injection or 200 days after initiation of the Phase I injection, followed by decreasing concentration until 350 days after Phase I injection (Figure 4). Subsequently, SF_5CF_3 concentration increased again, which is consistent with the SF_6 tracer curve (Figure 4). Please note that there are similar data gaps in the SF_5CF_3 record as a result of the pump failures. The double peaks in these tracer breakthrough curves are in agreement with previous tracer tests, suggesting that the storage formation consists of relatively homogenous porous media intersected by a low volume and fast flow path (i.e. fracture) that channels about 3% of tracer flow between the injection (HN02) and monitoring (HN04) wells (Khalilabad et al. 2008).

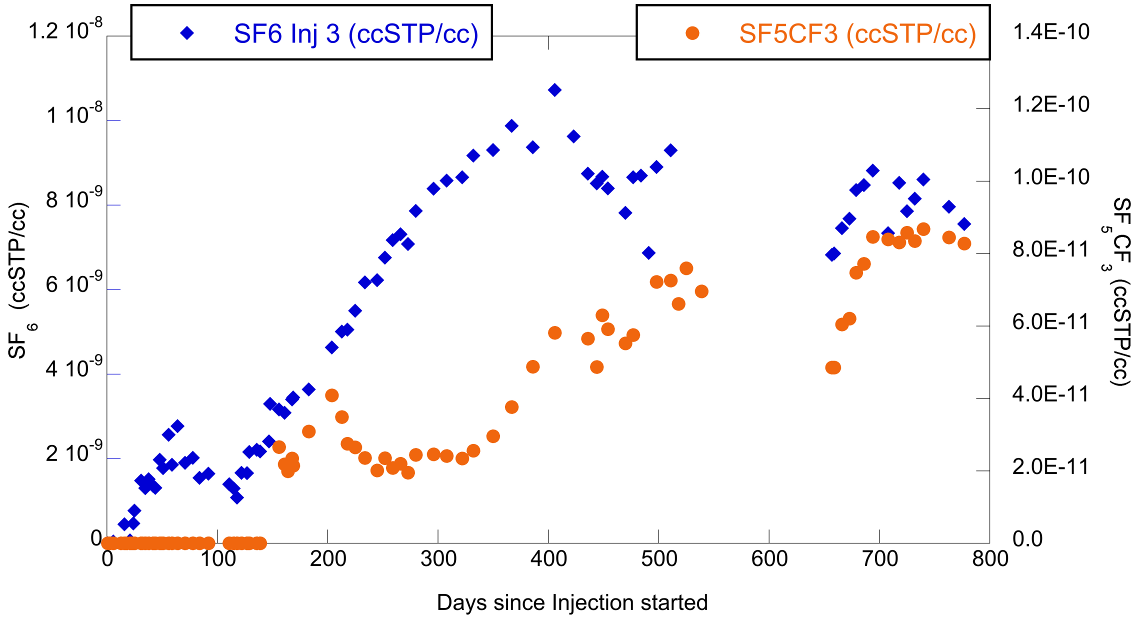

Figure 4. Time series of SF_6 (Phase I) and SF_5CF_3 (Phase II) concentrations (ccSTP/cc) vs. “Days since Phase I injection started” from monitoring borehole HN04. The major gap in data between 550 and 650 Days since injection started is due to submersible pump failure.

Task 3.0 Monitoring geochemical reactions and *in-situ* mineral carbonation with ^{14}C

The objective of this task was to tag the injected CO_2 with ^{14}C as a reactive tracer to monitor the fate of it in the storage reservoir. In combination with dissolved inorganic carbon (DIC) and ^{13}C analyses, CO_2-fluid-rock reactions can be characterized and the overall *in-situ* mineral carbonation can be defined.

Experimental Methods

The injected CO_2 was spiked with ^{14}C using a Na-$H^{14}CO_3$ stock solution that was injected into the injected water using a micro-metering pump (Figure 5).

Figure 5. $H^{14}CO_3$-solution storage tank (100 L) with micro-metering pump attached at the front. Amount of tracer solution injected was regulated by the injection system control system and depended on the actual CO_2/H_2O injection ratio in the injection borehole. Photo: J. Matter

For Phase I and Phase II injections, the ^{14}C concentrations of the injected CO_2 saturated water was 40.0 Bq/L ($^{14}C/^{12}C$: 2.16×10^{-11}) and 6 Bq/L ($^{14}C/^{12}C$: 6.5×10^{-12}), respectively (Table 1). The ^{14}C concentration in the reservoir prior to the injections was 0.0006 Bq/L or $^{14}C/^{12}C$ of 1.68×10^{-13}.

Fluid samples for ^{14}C and ^{13}C analyses were collected in 125 ml and 60 ml glass serum bottles, respectively. For ^{14}C analysis, water samples were acidified in a vacuum extraction system to release the dissolved inorganic carbon as CO_2. Carbon-14 concentrations were measured with ^{14}C-AMS in the W.M. Keck Carbon Cycle Accelerator Mass Spectrometery Laboratory at the University of California, Irvine and later in the BioAMS laboratory at Lawrence Livermore National Laboratory. Results are reported as fractions of Modern Standard, $\Delta^{14}C$, following the conventions of Stuiver and Polach (1977). All results are corrected for isotopic fractionation with $\delta^{13}C$ values measured on prepared samples using AMS spectrometer.

In addition, fluid samples for ^{13}C analysis were analyzed in the Environmental Isotope Laboratory at the University of Waterloo, Canada, using a conventional gas isotope mass spectrometer. The data are reported as $\delta^{13}C$ permil PDB.

The dissolved inorganic carbon (DIC) of each collected fluid sample was calculated using PHREEQC (Parkhurst and Appelo, 2013) from measured pH, alkalinity, *in-situ* temperature and total dissolved element concentration measurements. The pH was measured in the field with a Eutech Instruments TM

CyberScan pH 110 electrode calibrated using NBS standards and verified in the laboratory a few hours after sampling with a Cole Parmer glass pH electrode. Alkalinity titration was performed using the Gran function to determine the end point of the titration. The concentrations of elements were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using the SPEX Certified Reference standard at the University of Iceland. The overall uncertainty on calculated DIC measurements are estimated to be ±5%.

Results and Discussion

The time series of ^{14}C, DIC and pH from monitoring well HN04 are initially coincident with the SF_6 and SF_5CF_3 record with peak concentrations of ^{14}C and DIC around 56 days and 200 days after Phase I injection was initiated (Figures 6 and 7). The first peak is related to Phase I injection, whereas the second one at 200 days is the result of the Phase II injection. Subsequently, ^{14}C and DIC concentrations decreased and stayed more or less constant for the remaining monitoring period (Figure 6 and 7).

The similar initial pattern in the SF_6 and SF_5CF_3 tracer breakthrough curves and the ^{14}C and DIC time series suggest identical transport behavior of carbon and tracers in the storage reservoir. However, the subsequent decrease in ^{14}C and DIC concentrations is anti-correlated to the SF_6 and SF_5CF_3 data, which show increasing concentrations and a major breakthrough peak of the injected CO_2-saturated solution in monitoring well HN04 much later in the monitoring record (Figure 4). Based on the reactive tracer ^{14}C, it seems that most of the injected

CO_2 mass has not reached the monitoring well, whereas the bulk mass of the non-reactive tracers (SF_6, SF_5CF_3) has. Thus, the ^{14}C and DIC data strongly suggests that most of the injected CO_2 has been mineralized within the porous matrix of the basalt between the injection and monitoring well.

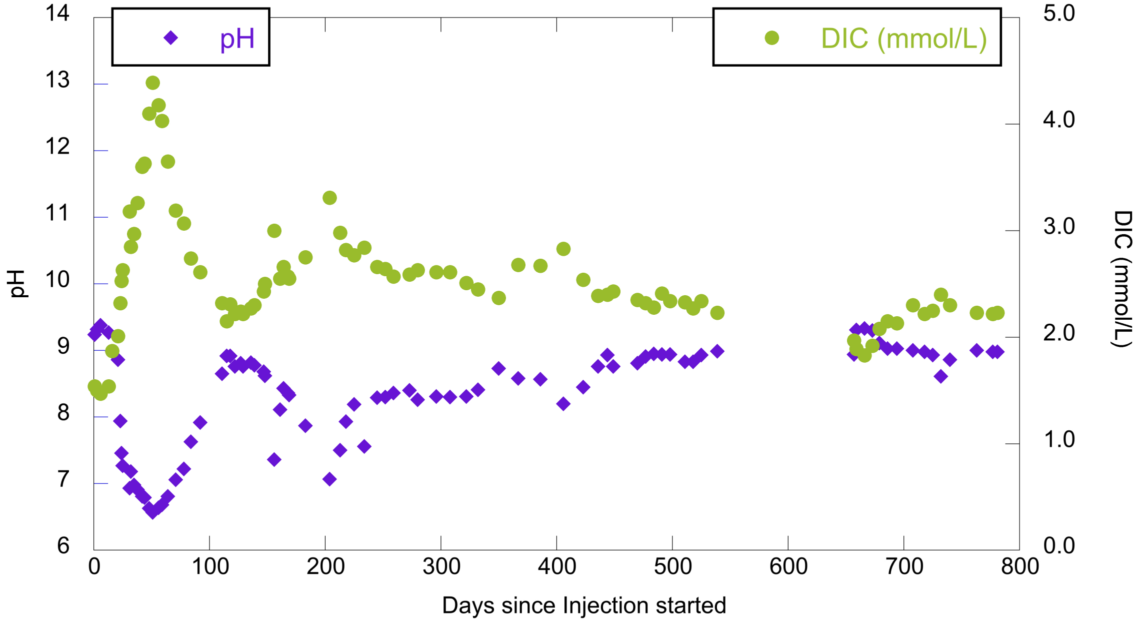

Figure 6. Time series of pH and total dissolved inorganic carbon (DIC in mmol/L) in monitoring borehole HN04 for Phase I and Phase II injections. The positive and negative peak in DIC and pH at ~200 Days since injection started, respectively, was caused by the Phase II injection.

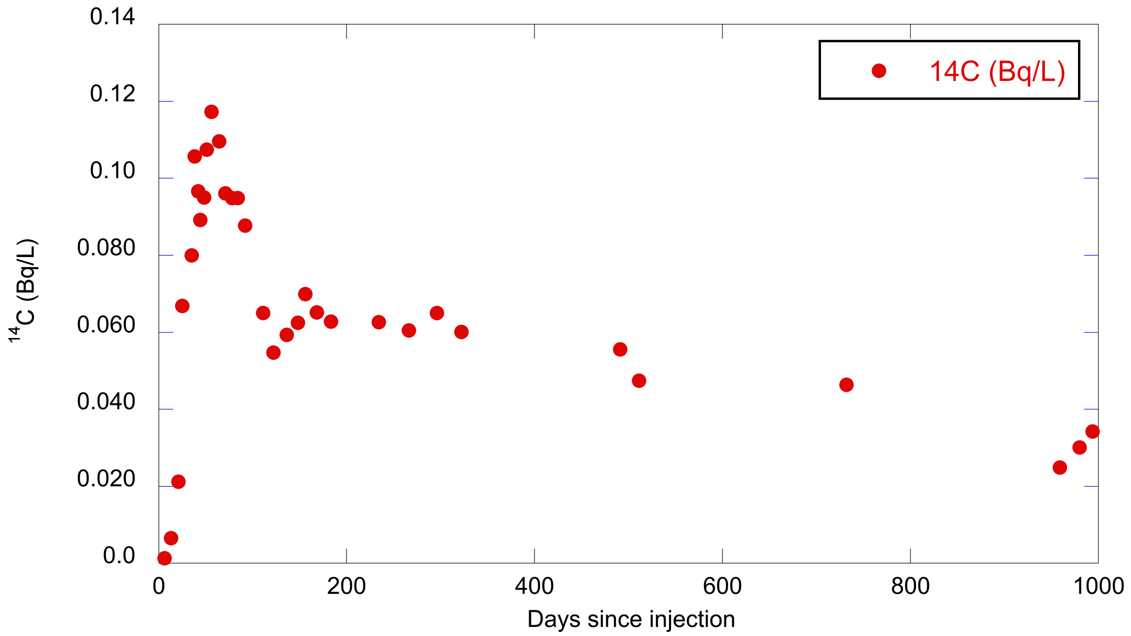

Figure 7. Time series of ^{14}C (Bq/L) in monitoring borehole HN04.

Task 4.0 Mineral carbonation studies on core samples

The objective of this task was to drill one 600 m deep borehole between the injection well (HN02) and the first monitoring borehole (HN04) at the CarbFix pilot injection site to retrieve rock core from the storage reservoir after the CO_2 injections in order to perform mineralogical and isotopic analyses on selected sub-samples from the core.

Experimental Methods

DTH air hammer and a tricone rotary technology were used to drill a 6 1/8” borehole down to 380 meters below surface in September 2014. Surface casing (7 5/8”) as well as a cemented liner were installed, the latter down to 380 m depth. Subsequently, wireline diamond coring, using a HQ 3.85" bit size, was conduced from 380 to 540.88 m to retrieve core samples between October and November 2014. Figure 8 and 9 show the drill hole design and actual wireline diamond drilling rig, respectively.

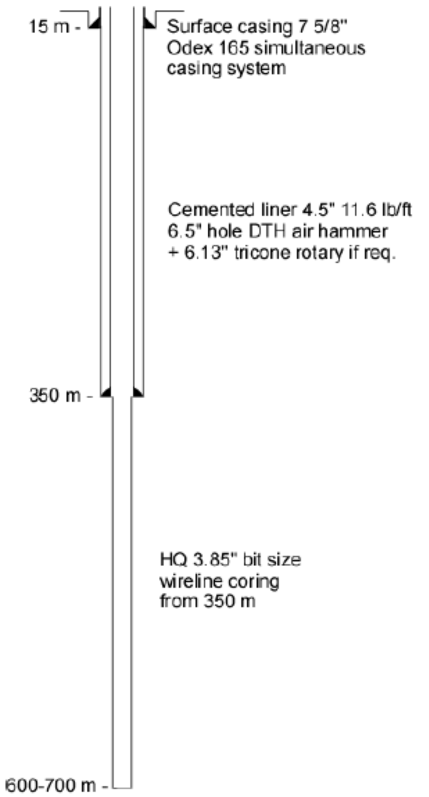

Figure 8. Well design for the KB-01 exploratory borehole at the CarbFix injection site. Courtesy of Raekto.

Raekto, an Icelandic drilling company, was in charge of well design, preparation of drilling platform, and to conduct the rotary drilling and wireline diamond coring. Orkuveita Reykjavikur (Reykjavik Energy) as the injection site owner was responsible for the onsite management during drilling. The responsible science party, led by J. Matter and M. Stute (Columbia University) conducted preliminary core description and sampling for microbiology at the drill site (Figure 10).

Figure 9. Wireline diamond drilling rig at the CarbFix injection site in October 2014. Photo: M. Stute.

Figure 10. Core description and collection of sub-core samples for microbiological and mineralogical analyses at the CarbFix injection site. Photo: J. Matter.

In addition, Matter and co-workers did quantitative core description a few months after drilling (Figure 11). This included a section log, description of lithology and phenocrysts, glass content, alteration, vesicle and vein logs, and description of secondary mineralogy in vesicles and veins.

Figure 11. Detailed core description and collection of sub-core samples for XRD, thin section and isotopic analyes. Photo: J. Matter.

We also collected a lot of sub-samples for mineralogical (XRD, SEM-EDXS) and isotopic analysis (carbon-14). For X-RAY diffraction and energy dispersive X-ray spectroscopy (EDXS) mapping performed at the Nanoscience Center at the University of Copenhagen. Samples were stored and treated in an anaerobic chamber to minimize oxidation. Measurements were conducted on a Bruker D8 DISCOVER equipped with a LynxEye detector and a Co-source. Scan range was 5-80° using a 0.05° step size and a count time of 10 s per step. SEM/EDXS measurements were conducted on a FEI Quanta 3D FEG SEM equipped with an Oxford instrument X-max 20 mm^2 EDXS detector having a nominal energy resolution of 0.125 keV for MnKa (FWMH). During imaging, accelerating voltage was 20 KeV and currents were 3.8 pA for SEM imaging and 8 nA for EDXS mapping. In the EDXS maps, color intensity for an element is linearly correlated with the integrated intensity measured in a narrow range round it characteristic X-ray (CaKa: 3.63-3.75 KeV; FeKa: 6.32-6.48 KeV; SiKa: 1.69-1.79 KeV; OKa: 0.49-0.56 KeV; CKa: 0.24-0.29 KeV; peak from CKa has a slight contribution of <5% from Au_N lines).

Results and Discussion

Wireline diamond drilling was completed on November 13, 2014. We successfully retrieved 174 m of core from the injection interval. Unfortunately, we could not recover the planned 200 m of core because the borehole collapsed at 500 depth during drilling. A 15-m long section was cemented to being able to continuing drilling. Unfortunately, the collapse of the drill hole resulted in the loss of the most interesting, highly fractured section, which has been recognized as one of the main groundwater flow zones in the target storage reservoir.

Core characterization and description shows that the upper section of the core is dominated by relatively compact hyaloclastite that was formed during a sub-glacier eruption. The lower sections are characterized by highly vesicular and denser basalt flows. Discrete, mainly steep fractures are generally intersecting the denser and more coherent basalt flow sections. Zeolites are the dominant secondary minerals in the vesicles whereas carbonate minerals (mainly calcite) either occur as individual crystals within the pore space or as secondary precipitates along the fracture surfaces (Figures 12 and 13). Veins and vein nets are taking up 0.8% of the core. Including the basaltic breccias this number increases to 3.5%. According to the vein log, the veins per m over the whole core is 8.1 veins/m of core and 0.7 carbonate veins/m. The carbonate vein frequency is generally quite low but there is a significant peak of 3.5 carbonate veins/m from 523.22 to 537.88 m depth (Table 2).

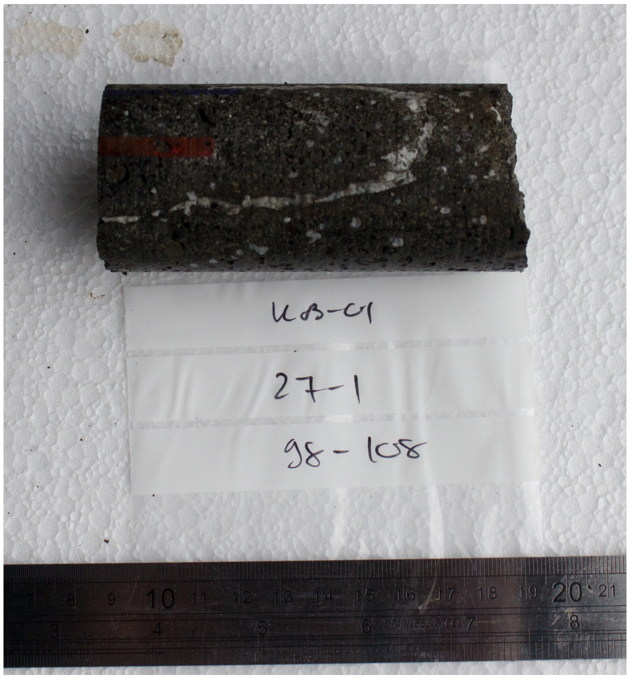

Figure 12. Sub-core sample of a steep fracture with calcite filling. Photo: J. Matter.

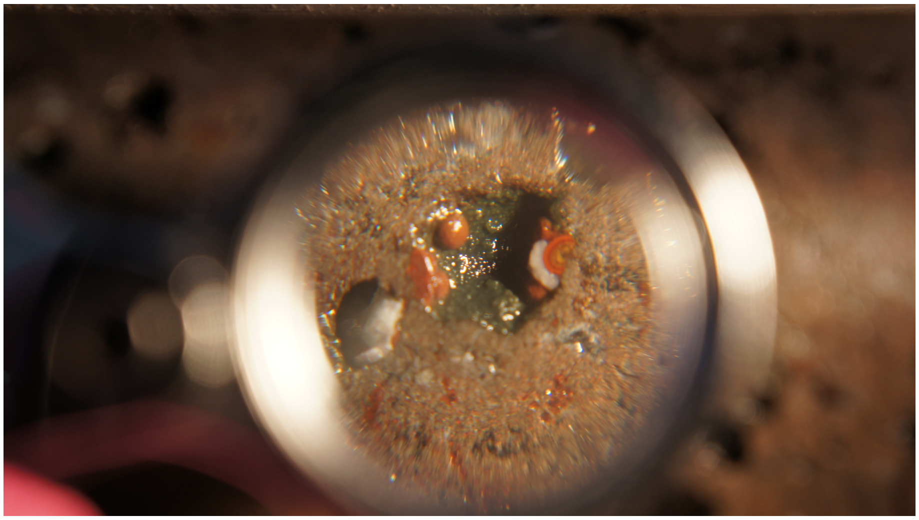

Figure 13. Generations of secondary mineralization in vesicles, magnified using a hand lens. Photo: B. Menez.

XRD and SEM-EDXS analyses of secondary minerals collected from the monitoring borehole (HN04) and the core samples reveal these precipitates to be dominantly calcite. The XRD analysis only shows the Bragg peaks expected for calcite (Figure 14) (e.g. Markgraf and Reeder, 1985).

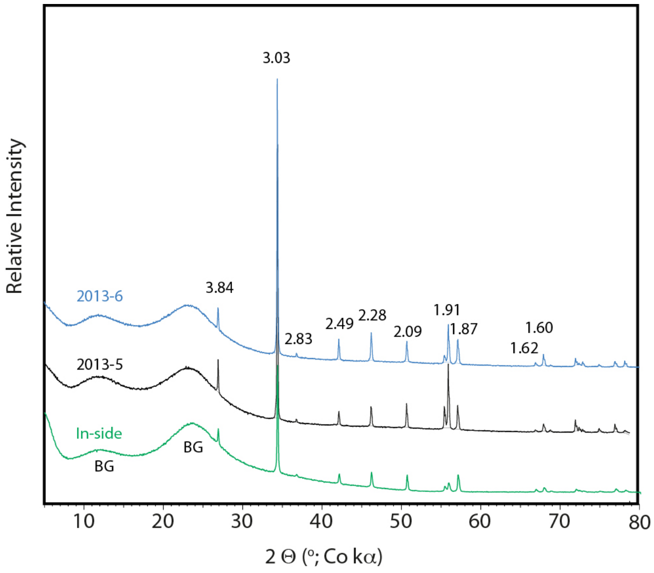

Figure 14. X-ray scans of sample 2013-5 and 2013-6 taken from the submersible pump in monitoring borehole HN04. The two broad peaks from the cap protecting the sample from further oxidation is marked BG. Courtesy of K. Dideriksen.

SEM images and EDXS mapping on the same samples clearly show 10 um to 1 mm elongated grains rich in Ca, C, and O, as we would expect for calcite. In addition, trace concentrations of Mg, Mn, and Fe were also analyzed (Figure 15). Generations of different secondary minerals were also found in the monitoring boreholes. EDXS mapping of the these samples show a banded structure where they were fractured (Figure 16), with a first generation of calcite containing material rich in Fe and Si, and a second generation largely with none of this material. This distribution of secondary minerals is in agreement with the fluid chemistry evolution during the injections, with Fe and Si ion activities high during the pure CO_2 injection and lower during the CO_2+H_2S injection.

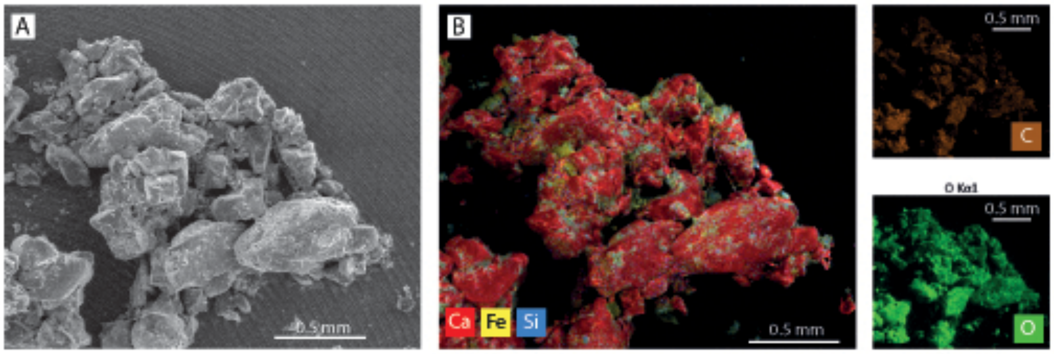

Figure 15. Overview SEM image (A) and EDX maps (B) of material recovered in monitoring borehole HN04. The maps for Ca, Fe and Si has been overlain the SEM image, whereas the maps for C and O are presented separately. Courtesey of K. Dideriksen.

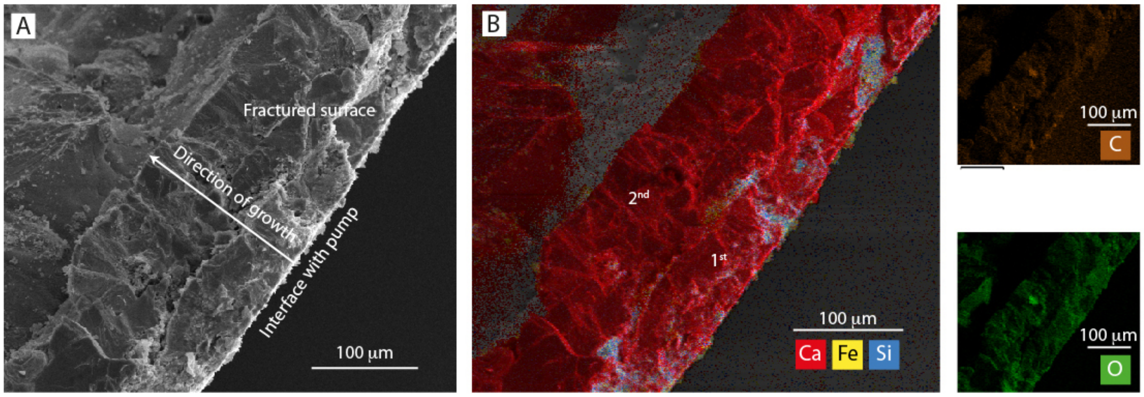

Figure 16. SEM images and EDX maps of fractured material from a mineral sample collected on the submersible pump in monitoring borehole HN04. (A) SEM image; direction of mineral growth is indicated. (B) EDX maps of are shown in SEM image. Maps for Ca, Fe and Si has been overlain the SEM image. Maps for C and O are presented separately. Courtesy of K. Dideriksen.

Radiocarbon analysis on secondary carbonate minerals recovered from the monitoring borehole (HN04) show a similarity in the ^{14}C concentration of the injected CO_2 and the precipitated secondary calcite. Carbon-14 values of the calcite are 7.48±0.8 and 7.82±0.05 fraction modern. Average ^{14}C concentration of the dissolved inorganic carbon in the monitoring borehole during the injections is 7.93±0.05 fraction modern. However, ^{14}C concentrations of secondary minerals collected from vesicles and fractures from the retrieved core sections are between 0.0±0.005 to 0.03±0.005 fraction modern. So far, we did not found any newly formed carbonate minerals in the 174 m of core that shows an elevated ^{14}C concentration similar to our injected solution. All the collected carbonate minerals and crystals are secondary minerals that were precipitated before our CO_2 injection. This is not a surprise. Carbonate minerals are quite abundant in basaltic rocks. Our sampling of discrete, fine grained carbonate from the core sections is biased and we might have missed the newly precipitated carbonates. Furthermore, we were not able to core the most important section of the injection reservoir due the collapse of the borehole during wireline coring.

Table 2. Summary core characterization logs of KB-01 borehole.

				Area of core = vein/vein net/rubble hosted secondary mineral								
Hole	**Core**	**Core top depth**	**cored**	**TOTAL**	**Saponite**	**Celadonite**	**CO_3**	**FeOx**	**SiO_2**	**Quartz**	**white Zeolite (thomsonite)**	**clear zeolite (chabasite)**
		mbsl	m	cm^2	cm^2	cm^2	cm^2	cm^2	cm^2	cm^2	cm^2	cm^2
KB-01	*1*	*366.75*	*6.1*	28.56	26.52	0.00	0.01	2.12	0.00	0.00	14.91	3.51
KB-01	*2*	*372.8*	*5.9*	5.38	6.28	0.00	0.00	3.37	0.00	0.00	4.03	2.80
KB-01	*3*	*378.75*	*6.0*	17.21	11.48	0.00	0.08	3.79	0.00	0.00	16.16	6.91
KB-01	*4*	*384.76*	*6.1*	3.46	4.26	1.62	0.00	1.68	0.00	0.00	1.93	1.05
KB-01	*5*	*390.86*	*5.9*	18.13	8.80	0.00	0.00	44.93	0.00	0.00	13.42	3.43
KB-01	*6*	*396.76*	*6.0*	7.17	13.67	0.01	0.00	6.29	0.00	0.00	0.78	0.28
KB-01	*7*	*402.72*	*6.1*	8.37	3.86	0.01	0.75	2.75	0.00	0.00	0.21	0.67
KB-01	*8*	*408.79*	*5.9*	24.45	10.08	0.00	4.18	6.17	0.00	0.00	0.00	0.00
KB-01	*9*	*414.72*	*7.8*	19.34	6.35	0.37	0.20	1.86	0.00	0.00	0.00	0.00
KB-01	*10*	*422.57*	*7.2*	20.02	9.46	0.00	0.33	2.67	0.00	0.00	0.00	0.00
KB-01	*11*	*429.79*	*5.8*	12.02	5.09	0.00	0.06	1.48	0.00	0.00	0.00	0.00
KB-01	*12*	*435.57*	*6.2*	6.58	5.61	0.00	0.04	0.93	0.00	0.00	0.00	0.00
KB-01	*13*	*441.74*	*6.0*	11.57	4.62	0.00	0.01	1.21	0.00	0.00	0.00	0.32
KB-01	*14*	*447.75*	*5.7*	22.32	10.13	0.00	0.43	3.77	0.00	0.00	0.00	1.26
KB-01	*15*	*453.47*	*6.1*	26.45	17.76	0.00	0.69	4.30	0.00	0.00	0.04	0.09
KB-01	*16*	*459.57*	*6.3*	12.07	7.56	0.00	0.12	2.18	0.00	0.00	0.00	0.00
KB-01	*17*	*465.89*	*6.0*	9.28	6.14	0.00	0.00	1.14	0.00	0.00	0.00	0.14
KB-01	*18*	*471.91*	*6.0*	16.54	9.51	0.00	0.66	3.97	0.00	0.00	0.96	0.29
KB-01	*19*	*477.92*	*6.8*	25.14	11.20	0.00	0.00	8.65	0.00	0.00	0.00	0.11
KB-01	*20*	*484.74*	*6.2*	22.02	14.30	0.00	0.30	5.85	0.00	0.00	0.00	0.00
KB-01	*21*	*490.94*	*5.9*	71.96	13.06	0.00	0.17	8.32	0.00	0.00	0.00	0.00
KB-01	*22*	*496.87*	*3.5*	8.17	6.31	0.00	0.00	1.50	0.00	0.00	0.00	0.00
KB-01	*23*	*500.41*	*6.4*	12.20	8.48	0.00	1.08	2.13	0.00	0.00	0.44	0.06
KB-01	*24*	*506.77*	*6.2*	22.00	13.48	0.00	0.01	7.46	0.00	0.00	0.00	0.00
KB-01	*25*	*512.95*	*6.2*	10.35	6.58	0.00	0.65	1.23	0.00	0.00	0.75	0.00
KB-01	*26*	*519.16*	*6.6*	7.78	2.95	0.00	0.78	1.07	0.00	0.00	2.44	0.00
KB-01	*27*	*525.76*	*6.5*	18.56	4.30	0.00	1.49	0.36	0.00	0.00	11.83	0.00
KB-01	*28*	*532.22*	*5.7*	80.39	17.30	0.00	17.68	0.11	0.00	0.00	20.12	0.00
KB-01	*29*	*537.88*	*3.0*	7.29	1.87	0.00	0.33	0.17	0.00	0.00	4.86	0.00

Task 5.0 Quantification of mineral carbonation in the CarbFix basalt storage reservoir

The main objective of this task was to quantify the mineralization of the injected CO_2 using the non-reactive and reactive tracers, and the dissolved inorganic carbon (DIC). Core and mineralogical samples from the wireline diamond drilled borehole (KB-01) were used as a confirmation of in-situ CO_2 mineralization and in support of the balance calculations.

Methods

Mass balance calculations for dissolved inorganic carbon (DIC) and ^{14}C were performed to assess in-situ mineralization of CO_2. The mixing fraction between the injected solution (IS) and the ambient groundwater (BW) in the storage reservoir was calculated for each extracted water sample (i) using

$$\left[SF_6\right]_i = X\left[SF_6\right]_{IS} + \left(1-X\right)\left[SF_6\right]_{BW} \tag{1}$$

with *X* being the fraction of injected solution in the extracted water sample. The expected DIC and ^{14}C values due to pure mixing was then determined from

$$DIC_{mix} = X \cdot DIC_{IS} + (1-X) \cdot DIC_{BW} \tag{2}$$

and

$$^{14}C_{mix} = X \cdot {}^{14}C_{IS} + \left(1-X\right) \cdot {}^{14}C_{BW} \tag{3}$$

The difference in DIC and ^{14}C concentration between the measured values measured in retrieved fluid samples and the expected values assuming only mixing between injectate and ambient groundwater yield the loss of DIC and ^{14}C due to carbonate precipitation.

Results and discussion

Applying the above discussed mass balance equations, the resulting DIC and ^{14}C concentrations are much larger than the measured ones in the collected water samples, suggesting a loss of DIC and ^{14}C along the subsurface flow path between the injection (HN02) and monitoring (HN04) boreholes. The most logical mechanism for this difference is carbonate precipitation. The difference between the calculated and measured DIC and ^{14}C indicate that between 95 and 98% of the injected CO_2 was mineralized through water-CO_2-basalt reactions within two year (Figure 17 and 18). The initial peak concentrations in DIC and ^{14}C detected around 56 days after injection (Figure 6 and 7) suggest that solute travel time along the low volume fast flow path was too short for significant CO_2 mineralization to occur. Most of the injected CO_2 was likely mineralized within the porous matrix of the basalt that allows for longer fluid residence times and thus extended reaction time.

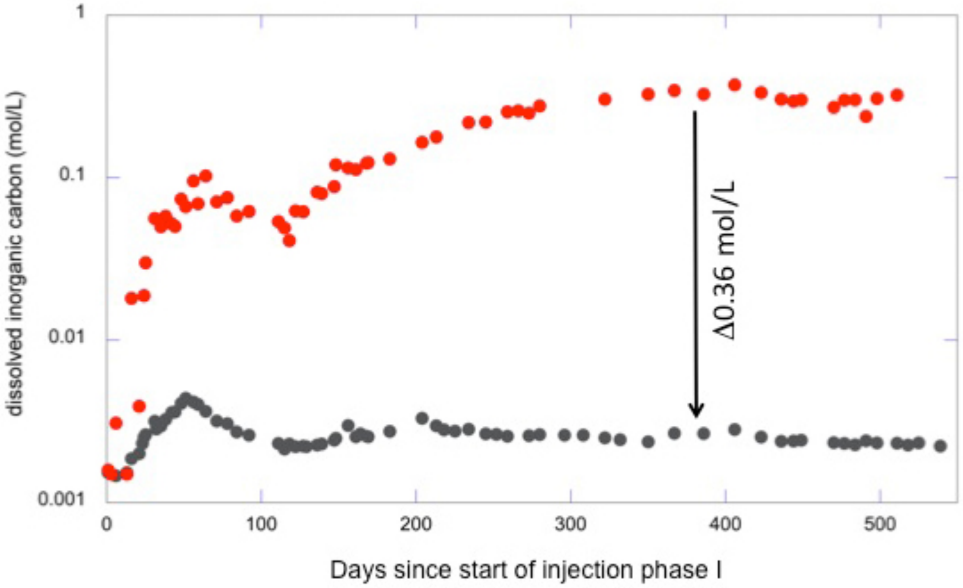

Figure 17. Time series of expected (red circle) versus measured (grey circles) dissolved inorganic carbon concentration (DIC, mol/L) in monitoring borehole HN04. The data indicates that >98% of injected dissolved CO_2 has been trapped in mineral form in less than 2 years.

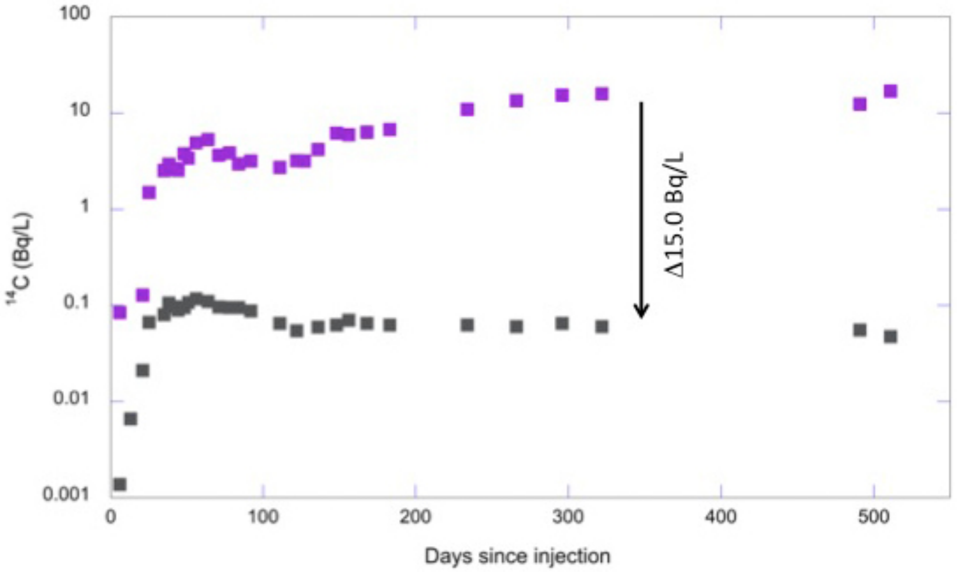

Figure 18. Times series of expected (purple squares) versus measured (grey squares) ^{14}C concentration (Bq/L) in monitoring borehole HN04. The data indicates >95% conversion of injected CO_2 to carbonate minerals.

Calculated differences between DIC and ^{14}C concentrations between the values measured in the extracted fluid samples and the theoretical mixing values yield a loss in DIC and ^{14}C (negative values), which is consistent with carbonate precipitation (Figure 19). Dissolution of pre-existing carbonate minerals in the storage reservoir would result in an increase in DIC and a decrease in ^{14}C in the remaining fluid.

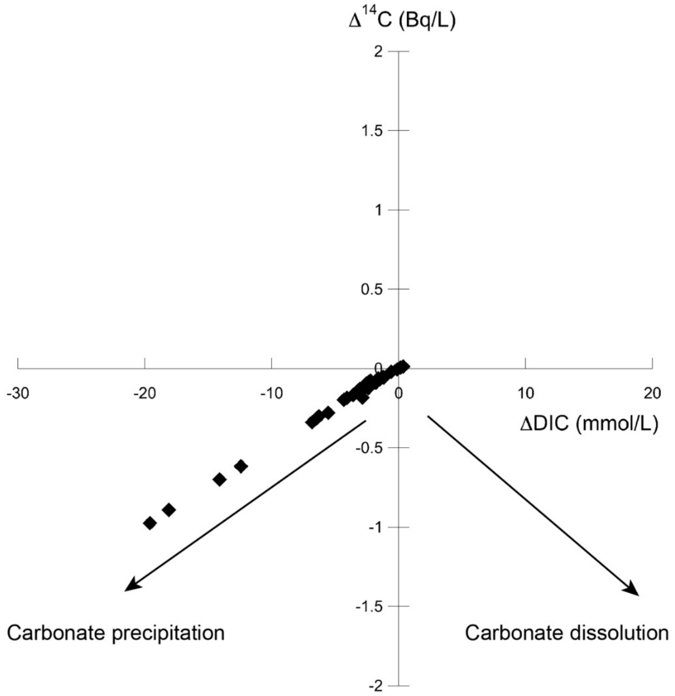

Figure 19. ΔDIC vs. $\Delta^{14}C$ of retrieved fluid samples. Negative values confirm precipitation of carbonate minerals.

Carbonate precipitation is also confirmed by calculated fluid saturation states of retrieved fluid samples, showing that the storage reservoir fluid are at saturation or supersaturation with respect to calcite at all times except during the very initial low volume flow path contribution. XRD and SEM-EDXS analyses of secondary precipitates also show calcite and ^{14}C concentrations of the injected CO_2 is similar to the ^{14}C concentration of precipitated calcite collected in the monitoring borehole (HN04).

CONCLUSIONS

The project goal was to demonstrate in situ mineralization of CO_2 in basaltic rocks using ^{14}C as a reactive tracer. The project team successfully demonstrated for the first time the permanent and safe disposal of CO_2 as carbonate minerals in basaltic rocks. We showed that between 95 and 98% of the injected CO_2 was mineralized to carbonate minerals in less than two years after its injection. Till now, the common view has been that mineral trapping in geologic CO_2 storage reservoirs takes several hundreds to thousands of years. However, our results proof that mineral trapping in basaltic rocks is far faster than previously postulated. The fast conversion rate of CO_2 to calcite minerals in the CarbFix storage reservoir is the result of several key processes:

(1) The newly developed CO_2 injection system that injected water-dissolved CO_2 into the subsurface instead of CO_2 gas. CO_2 dissolved in water facilitates fast water-rock reactions and thus fast CO_2 mineralization.
(2) The relatively fresh and glassy basalt at the CarbFix injection site exhibits relatively fast mineral dissolution rates.

(3) Mixing of injected water with a pH of 3.2 with alkaline ambient formation waters (pH 8.9 - 9.8) led to an initial neutralization of the injected acidic CO_2-saturated solution subsequently supporting the precipitation of carbonate minerals at more neutral to alkaline pH conditions.

The research showed that combining non-reactive and reactive tracers allows for quantitative monitoring and verification of dissolved and mineralized CO_2, which is not possible with other more conventional (geophysical) monitoring techniques. Non-reactive tracers, such as SF_6 and SF_5CF_3 are relatively inexpensive, detectable to ppb levels and easy to inject into a CO_2 gas stream. Both tracers indicated the bulk arrival of the injected solutions several months after the injection. Using these non-reactive tracers, we were able to distinguish between a low volume fast flow path along fractures and the high volume slow flow path in the basaltic matrix, and to quantify mixing between ambient reservoir fluid and injected solutions.

Furthermore, the project successfully demonstrated the continuous and accurate tagging of the injected CO_2 with ^{14}C at parts per trillion levels. However, the ^{14}C tagging system, developed and used during this project, involved the storage of a ^{14}C-enriched (10 mCi) $H^{14}CO_3$ stock solution of 100 liters in a stainless steel tank, which requires specific safety features. Developing and applying a tagging system that involves miniscule quantities of ^{14}C-tagging material is certainly recommended. Nevertheless, tagging the injected CO_2 with ^{14}C allows for direct and unique verification of solubility and mineral trapping of CO_2 in geologic reservoirs. Mass balance calculations using dissolved inorganic carbon (DIC) and ^{14}C reveal that only minor amounts of the ^{14}C tracer reached the observation borehole along the low volume fast flow path at the CarbFix injection site. Thus, most of the injected CO_2 has been taken out of the reservoir most likely via CO_2 mineralization to carbonate minerals. Results from the mass balance calculation using DIC or ^{14}C are in good agreement, revealing 95 or 98% CO_2 mineralization, respectively.

Secondary mineral precipitates collected from the monitoring borehole HN04 confirm CO_2 mineralization. These precipitates are dominantly calcite, as confirmed by XRD and SEM-EDXS analyses. Furthermore, the calcite is enriched in ^{14}C, similar to the dissolved inorganic carbon of the reservoir fluid during the CO_2 injection. Characterization of the 174-m long core collected from the injection interval shows that 0.8% of the whole cores are veins or vein nets with on average only 0.7 carbonate veins per meter of core. Carbon-14 analysis of secondary carbonate minerals from fracture surfaces and vesicles reveal low ^{14}C values between 0.0±0.005 to 0.03±0.005 fraction modern, which is typical of pre-existing (pre-CO_2 injection) carbonate minerals. These results suggest that we might have missed the secondary carbonate minerals precipitated from the injected CO_2. However, it is quite possible that we lost the opportunity to sample the newly precipitated carbonates during drilling because of a borehole collapse at 500 m depth. According to our geophysical borehole logs, the main permeable zone in the target storage reservoir is between 500 and 520 m depth. It is likely that most of our injected CO_2 saturated solution was transported in this zone.

Subsequently the Phase I injection, the plan was to conduct a continuous combined injection of the major flue gases, CO_2 and H_2S, of the Hellisheidi geothermal power plant in the same storage reservoir. The main objective of the Phase II injection was to study the feasibility of a mixed gas injection, which would significantly lower the cost of gas separation. However, we had to stop the mixed gas injection after 6 months due to injectivity issues in the injection borehole. The team's monitoring results from the injection borehole revealed that the injection of CO_2 and H_2S in the relatively shallow storage reservoir (low temperature) stimulated the growth of biofilms and the precipitation of iron-oxyhydroxides. Therefore, the recommendation is to inject the CO_2 and H_2S flue gas mixture into the deeper (i.e. hotter; ~170 - 200°C) geothermal reservoir to avoid any interaction with biology.

In summary, the project demonstrated rapid permanent storage of CO_2 in basaltic rocks via mineral trapping. The project also demonstrated the feasibility of ^{14}C-tagging for the monitoring and verification of geological CO_2 storage. Tagging the injected CO_2 with ^{14}C in combination with non-reactive tracers such as SF_6 and SF_5CF_3 allowed an unambiguous conclusion that a significant fraction of the injected CO_2 had been converted to carbonate minerals via CO_2-fluid-rock reactions. Thus, the project has defined the foundation of rapid mineral trapping of CO_2 in basaltic storage reservoirs and of ^{14}C tagging for quantitative monitoring and verification of geologic CO_2 storage.

GRAPHICAL MATERIAL LIST

Table of Figures:

Table of Tables:

BIBLIOGRAPHY

Alfredsson, H. A., et al., Int. J. Greenhouse Gas Control 12, 399-418 (2013).

Aradottir E. S., et al., Int. J. Greenhouse Gas Control 9, 24-40 (2012).

Bachelor, P. P., et al., J. Radioanal. Nucl. Chem. 277(1), 85-89 (2008).

Bachu, S., W. D. Gunter, E. H. Perkins, Energy Conversion and Management 35(4), 269-279 (1994).

Benson, S. M., E. Gasperikova, G. M. Hoversten, IEA Greenhouse Gas R&D Program Report (2004).

Clark, I. D., P. Fritz, Environmental Isotopes in Hydrogeology (Lewis Publisher, Boca Raton, New York, 1997).

Goldberg, D. S., T. Takahashi, A. L. Slagle, PNAS 105(29), 9929-9925 (2008).

Hoversten, M., et al., Proceedings of the 8th International Workshop on Greenhouse Gas Technology, Trondheim, Norway, June 19-22.

Hovorka, S. D., et al., Environmental Geosciences 13(2), 105-121 (2006).

Lackner, K. S., S. Brennan, Climatic Change 96, 357-378 (2009).

Markgraf, S. A., R. J. Reeder, American Mineralogist 70, 590 (1985).

Matter, J. M., P. B. Kelemen, Nature Geoscience 2, 837-841 (2009).

Mayer, B., et al., Int. J. Greenhouse Gas Control 16, S177-184 (2013).

Metz, B., O. Davidson, H. de Coninck, M. Loos, L. A. Meyer, Eds. IPCC Special Report on Carbon Dioxide Capture and Storage (Cambridge Univ. Press, New York, 2005).

Parkhurst, D. L., C. A. J. Appelo, Description of input and examples for PHREEQC version 3, U.S. Geological Survey Techniques and Methods, book 6, 497 pp. (2013).

Schaef, H. T., B. P. McGrail, A. T. Owen, Int. J. Greenhouse Gas Control 4, 249-261 (2010).

Sigfusson, B., et al., Int. J. Greenhouse Gas Control 37, 213-219 (2015).

Stuiver, M., H. A. Polach, Radiocarbon 19(3), 355-365 (1977).