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Monitoring permanent CO₂ storage by in situ mineral carbonation using a reactive tracer technique

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Abstract

In situ mineral carbonation provides the most effective and permanent solution for geologic CO₂ storage. Basaltic rocks have the potential to store large volumes of CO₂ as (Ca, Mg, Fe) carbonates [1]. Existing monitoring and verification techniques for geologic CO₂ storage are insufficient to quantitatively characterize solubility and mineral trapping in a geologic reservoir. We developed and tested a new reactive tracer technique for quantitative monitoring and detection of dissolved and chemically transformed CO₂. The technique involves the active tagging of the injected CO₂ with low levels of radiocarbon (¹⁴C) as a reactive tracer in combination with the injection of non-reactive tracers such as sulfurhexafluoride (SF₆) and trifluoromethylsulphur pentafluoride (SF₅CF₃). The tracer technique has been applied at the CarbFix pilot injection site in Hellisheidi, Iceland as part of a comprehensive geochemical monitoring program during two injection phases; Phase III and IV. SF₆ and SF₅CF₃ confirm the arrival of the injected CO₂ and CO₂+H₂S solutions at the first observation well HN04, which is 125m west of the injection well at 520 m depth. The initial breakthrough of the migrating dissolved CO₂ front occurred 63 and 62 days after injection began as evidenced by an initial peak in the SF₆, SF₅CF₃, ¹⁴C, and dissolved inorganic carbon (DIC) concentrations. The major increase in the non-reactive tracer concentrations occurred several months after the initial breakthrough, although no major concentration increase has been observed for ¹⁴C and DIC suggesting that mineral reactions are dominant during CO₂ injection.

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1. Introduction

Geologic storage (disposal) of CO₂ has been proposed to reduce CO₂ emissions in a fossil-fuel based economy [e.g. 2, 3]. Conventionally, dry CO₂ is injected into reservoirs at depths where CO₂ is in a supercritical state (>800 m depth). At this depth, injected CO₂ is expected to be stored as a buoyant fluid in contact with reservoir brines, reservoir rocks and caprock formations. The buoyancy of the supercritical CO₂ requires high integrity of the caprock formation, which can degrade as a result of CO₂-fluid-rock reactions. Thus, the success and effectiveness of geologic CO₂ storage depends on reservoir and caprock stability, the retention time and the risk of leakage [4]. An alternative storage approach is to inject CO₂ dissolved in water into unconventional reservoirs such as basalt, thereby reducing its buoyance and increasing its reactivity with reactive reservoir rocks [5, 6]. As demonstrated in previous laboratory studies, basalt and ultramafic rocks have a high reactivity with CO₂, enabling the mineralization of CO₂ to stable carbonate minerals such as calcite, magnesite, dolomite and siderite [e.g. 7, 8, 9].

Geologic CO₂ storage in supercritical or dissolved form requires monitoring, verification and accounting to ensure the safety and permanence of CO₂ storage. Existing monitoring techniques such as seismic or electromagnetic imaging are insufficient to quantitatively characterize CO₂ stored in dissolved (solubility trapping) or in mineral (mineral trapping) form. In contrast, geochemical monitoring techniques using non-reactive and reactive tracers are useful for directly monitoring the dynamics and reactivity of the injected CO₂ and mobile formation fluids. The varieties of tracers are transported differently, and measurement of their concentrations and changes in their ratios can be used to quantitatively characterize physical and geochemical processes at field scale. In this paper, we discuss the development of a new reactive tracer technique for quantitative monitoring and detection of dissolved and chemically transformed CO₂ and present results from the CarbFix pilot injection site in Hellisheidi Iceland, where this new technique has been tested and applied for CO₂ storage in basalts.

2. CarbFix Pilot Injection Site

The CarbFix project in Iceland was designed to study the feasibility of CO₂ storage in basaltic rocks by in situ mineral carbonation. It is a fully integrated CO₂ storage project involving the capture and separation of flue gases from the Hellisheidi geothermal power plant, the transportation of gases to the injection site via a ~3km long pipeline, the injection of the gases, and the monitoring and verification of the storage. The injection site is located in SW Iceland, 30 km east of Reykjavik. The power plant produces up to 40,000 tons of CO₂ and 16,000 tons of H₂S per year as a byproduct of the geothermal energy production [10]. The injection site is equipped with a 2000 m deep injection well (HN02, cased from the surface to 400 m) and 12 monitoring wells ranging in depth from 150 to 1300 m (Fig.1) [11]. The target injection and storage formation between 400 and 800 m depth consist of fine to medium grained basaltic lava flows of olivine tholeiite composition [11]. The injection formation is overlain by a hyaloclastite formation of consolidated volcanic ash (Fig. 1). The lateral and intrinsic permeability of the injection formation is 300 and 1700x10⁻¹⁵ m², respectively [12]. The ambient groundwater at injection depth has a temperature of 33°C, a pH ranging from 8.4 to 9.4, and a pCO₂ below atmospheric [11].

Two injection tests have been conducted at the CarbFix injection site. In January 2012, 175 tons of pure CO₂ was injected fully dissolved in water (~5000 tons) at a fluid injection rate of 1800 gs⁻¹ using a new injection system that was developed by the CarbFix research community and installed in injection well HN02 to allow for co-injection of water and gases [6]. CO₂ was supplied from a 30-m³ tank, whereas co-injected water was pumped from a water well that is situated close at the injection site. This phase is referred as the Phase III injection. In July 2013, 73 tons of a CO₂+H₂S mixture (Phase IV injection) was co-injected with water (~2500 tons) into the same target formation using the same injection well. During Phase III and IV CO₂ was fully dissolved at injection depth, and the dissolved inorganic carbon concentration (DIC) of this single phase CO₂-rich solution was 0.82 mol/L at injection depth [6].

The geochemical monitoring program involved the continuous injection of SF₆ and ¹⁴C during Phase III and SF₅CF₃ and ¹⁴C during Phase IV, respectively. SF₆ and SF₅CF₃ were mixed into the CO₂ and CO₂+H₂S flue gas

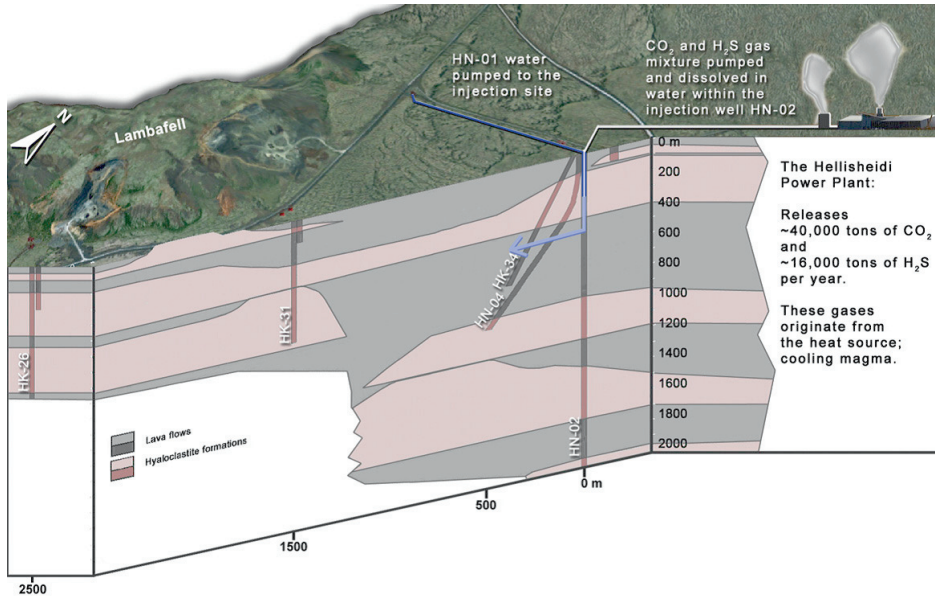


Fig. 1. Geological cross-section of the CarbFix injection site. CO₂ and H₂S are injected fully dissolved in water in injection well HN02 to a depth of 540 m. Fluid samples are collected in observation wells downstream from the injection well for monitoring and verification of the dissolved gas injection (modified from [11]).

stream at the power plant using a mass flow controller, whereas calibrated amounts of a H¹⁴CO₃⁻ solution was dynamically added to the water injection stream. The purpose of adding the H¹⁴CO₃⁻ solution to the injection stream was to label the injected CO₂ with ¹⁴C, which allows us to distinguish between the injected CO₂ and native carbon in the storage reservoir. Native carbon in typical CO₂ storage reservoirs has generally low ¹⁴C concentrations or is ¹⁴C dead. During geochemical processes, such as precipitation of carbonate minerals, the solid phase will get enriched in the heavier carbon isotopes (¹³C and ¹⁴C) and the remaining dissolved carbon will become isotopically lighter. Since ¹⁴C is only minimally affected by isotope fractionation during phase transition relative to its precision of measurement [13], it is an ideal tracer to characterize and quantify CO₂-fluid-rock reaction and thus mineral carbonation.

Fluid and gas samples are obtained at the wellhead at the observation wells using pre-installed submersible pumps, and in-situ in the injection well using a bailer system. Sampling occurs at regular intervals during and post Phase III and IV injections. Prior to the injections, fluid samples were collected and analyzed to define baseline chemical composition and tracer concentrations of the ambient groundwater in the target storage reservoir. Concentrations of SF₆ and SF₅CF₃ are measured by gas chromatography and ¹⁴C_{DIC} by accelerator mass spectrometry (AMS). Dissolved inorganic carbon concentration (DIC) is calculated for each sample using alkalinity and pH, which were measured at in-situ conditions.

3. Results and discussion

The field team began collecting fluid samples in the observation wells on January 24, 2012 when the pure CO₂ injection began. Only results from observation well HN04, which is 10m west of the injection well at the surface and 125m at 520 m depth, are discussed herein. So far, over 150 fluid samples have been collected in HN04 and analyzed for tracer concentrations.

Figure 2 shows the SF₆ and SF₅CF₃ concentrations in HN04 as a function of time (days since start of Injection Phase III). Initial breakthrough of the CO₂-rich fluid occurred 63 days (March 27, 2012) after injection as indicated

by an initial peak in SF₆ concentration. Initial breakthrough of the CO₂+H₂S-rich fluid was 62 days (August 16, 2012) after injection as shown by the SF₅CF₃ curve (Fig. 2). After the initial breakthrough peaks, SF₆ and SF₅CF₃ concentrations are decreasing a little bit before a constant increase in their concentrations is observed in HN04. Peak concentration of SF₆ was reached on day 404 (March 4, 2013) followed by a continuous decrease, whereas SF₅CF₃ concentration is still increasing (Fig. 2). The data gap between 550 and 650 days since the start of injection of Phase III is due to a failure of the submersible pump in HN04.

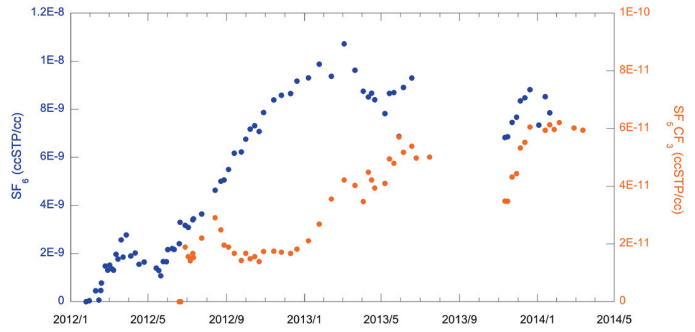


Fig. 2. Time series of SF₆ and SF₅CF₃ tracer concentrations (ccSTP/cc) in observation well HN04 for injection Phase III and IV.

The initial breakthrough of the SF₆ and SF₅CF₃ confirms previous tracer test data. Khalilabad et al. [14] conducted slug type tracer tests using sodium fluorescein at the CarbFix injection site to study the regional hydrology prior to CO₂ injection. Based on a one dimensional and multipath tracer dispersion model, a low volume and fast flow path was found to channel approximately 3% of the tracer flow between the injection well HN02 and observation well HN04. The model also predicts that most of the storage formation consists of a large volume of relatively homogeneous porous media. This fast flowing and low volume flow path is also indicated by the SF₆ and SF₅CF₃ breakthrough curves with initial peak concentrations at around 60 days after injection. The bulk of the injected solution, however, reaches HN04 much later, suggesting a more tortuous flow path within the rock matrix.

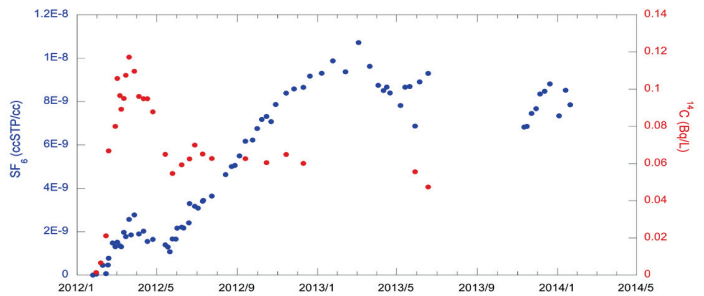


Fig. 3. Time series of SF₆ (ccSTP/cc) and ¹⁴C (Bq/L) tracer concentrations in observation well HN04 for injection Phase III and IV.

The concentration of the reactive tracer ¹⁴C in HN04 reveals the same initial breakthrough occurring ~59 days (March 23, 2012) after injection, as shown by a peak in ¹⁴C concentration, followed by decreasing concentration for the remaining monitoring record (Fig. 3). Similarly, fluid sample analysis shows an increase in the DIC to maximum 4.39E-03 mol/L in March 2012 (51 days after pure CO₂ injection), coincident with the initial rise in SF₆ and ¹⁴C concentrations (Fig. 4). A second, minor peak in DIC was observed in end of August 2012, which is concomitant with the initial peak in SF₅CF₃ concentration. Thus, the slight increase in DIC at this time is related to the CO₂+H₂S injection. After that, no further significant increase in DIC has been observed for the remaining monitoring record.

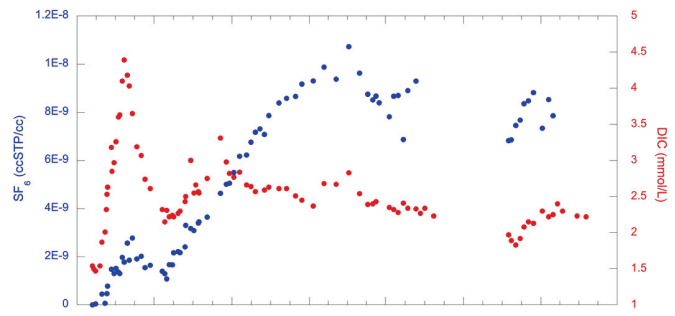


Fig. 4. Time series of SF₆ (ccSTP/cc) and DIC (mmol/L) concentrations in observation well HN04 for injection Phase III and IV.

The major rise in SF₆ and SF₅CF₃ concentrations after their initial peak concentrations indicate the bulk arrival of the injected solution of Phase III and IV. However, the ¹⁴C and the DIC concentrations remain consistently low

except during the initial breakthrough phase. This indicates that most of the injected dissolved CO₂ has not reached the observation well, suggesting that it reacted with the basaltic rocks along the flow path between the injection and observation wells within one year (Fig. 4). Thus, the travel time between the two wells is long enough for most of the injected CO₂ to react with the basalt. However, the travel time along the low volume, fast flow path was too short for the CO₂ to react with the basalt.

Monitoring for Phase III and IV is still going on at the injection site, which will allow us to establish the full breakthrough curves of the non-reactive and reactive tracers and to calculate an overall carbon mass balance. In addition, coring into the injection interval in October 2014 will allow us to retrieve rock samples, which may provide additional, crucial information about CO₂-basalt reactions and the precipitation of carbonate minerals.

4. Summary

In situ mineral carbonation in basalt offers the potential for permanent CO₂ storage in form of environmentally benign carbonate minerals. This potential has been evaluated at the CarbFix pilot injection site in SW Iceland, where two CO₂ injection tests (Phase III and Phase IV injection) occurred in 2012. Phase III involved a 175 tons of CO₂ injection in January 2012 and Phase IV a 73 tons of CO₂&H₂S mixture, respectively. In both cases, the gases were injected fully dissolved in water into the target storage formation between 400 and 800 m depth. A new reactive tracer technique, which involves the tagging of the injected CO₂ with ¹⁴C, has been developed and applied in combination with non-reactive tracers such as SF₆ and SF₅CF₃ in order to directly monitor and characterize solubility and mineral trapping. In both experiments the injected CO₂-enriched solution was successfully detected and characterized by tracer detection. SF₆ and SF₅CF₃ indicate the bulk arrival of the injected solutions several months after the injection. C-14 reveals that only a minor amount of this reactive tracer reached the observation well HN04 along the low volume fast flow path between the injection well HN02 and HN04. This is confirmed by the DIC concentration that remains close to background (pre-injection) after the initial peak arrival of the injected solutions. The initial results summarized above demonstrate fast reactions of the injected CO₂ with basalt.

Acknowledgements

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