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<p>SUMMARY:</p> <p>The CarbFix CO₂ storage pilot project in Iceland has been established to investigate the potential for mineral carbon storage in basalt as a solution to reducing CO₂ emissions in the atmosphere. Conceptually, CO₂-saturated waters would enhance basalt dissolution due to its low pH, thus releasing primarily divalent cat-ions into the solution. Stable carbonate minerals, such as CaCO₃, MgCO₃, FeCO₃, and mixtures thereof, would then precipitate during the CO₂-charged water-basalt interactions. A novel high pressure column flow reactor (HPCFR) was built to investigate the evolution of fluid and solid chemical composition along a 2.3 meter flow path. The scale of the HPCFR, the ability to sample a reactive fluid at discrete spatial intervals under pressure and the possibility to measure the <i>in situ</i> dissolved inorganic carbon and pH, all render the HPCFR unique in comparison with other reactors constructed for studies of CO₂-charged water-rock interaction. The current and future HPCFR experiment will be carried out as a part of NORDICCS training and its aim is to reach favourable conditions for secondary mineral precipitation. Data obtained during this study will result in better understanding of mineral replacement reactions occurring during underground CO₂ storage in basaltic terrains.</p> <p>KEYWORDS: Mineral precipitation, storage pilot, basalt, cat-ions, Iceland</p>	

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An experimental study of basaltic glass–H₂O–CO₂ interaction with a high pressure column flow reactor

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Abstract

The CarbFix CO₂ sequestration pilot project in Iceland has been established to investigate the potential for mineral carbon storage in basalt as a solution to reducing CO₂ emissions in the atmosphere. Conceptually, CO₂-saturated waters would enhance basalt dissolution due to its low pH, thus releasing primarily divalent cations into the solution. Stable carbonate minerals, such as CaCO₃, MgCO₃, FeCO₃, and mixtures thereof, would then precipitate during the CO₂-charged water–basalt interactions. A novel high pressure column flow reactor (HPCFR) was built to investigate the evolution of fluid and solid chemical composition along a 2.3 meter flow path. The scale of the HPCFR, the ability to sample a reactive fluid at discrete spatial intervals under pressure and the possibility to measure the *in situ* dissolved inorganic carbon and pH, all render the HPCFR unique in comparison with other reactors constructed for studies of CO₂-charged water–rock interaction. The current and future HPCFR experiment will be carried out as a part of Nordiccs training and its aim is to reach favourable conditions for secondary mineral precipitation. Data obtained during this study will result in better understanding of mineral replacement reactions occurring during underground CO₂ storage in basaltic terrains.

Introduction

Mineralization of carbon dioxide is the final product of CO₂ geological storage which provides long-term stability for sequestered CO₂. The relative amount of fixed CO₂ and the rate of mineralization depend on the rock type, injection methods and temperature. A conceptual model of CarbFix CO₂ storage project established in Iceland (Gislason et al., 2010; 2014) assumes that acidic carbonated waters injected into basaltic rocks will initially enhance rock dissolution through the consumption of proton and release divalent cations such as Ca²⁺, Mg²⁺, and Fe²⁺ into the aquifer or pore space. As reactions progress, the pH rises and these cations combine with CO₃²⁻ to precipitate as carbonates (Gislason et al., 2010).

In order to better understand and model processes which happen in the reservoir during CO₂–water–basalt interaction over time, a high pressure column flow reactor (HPCFR) was built and tested as a part of CarbFix. This medium scale 2.3 m long reactor provides an opportunity to study the rate of basaltic rock dissolution and solid replacement reactions under controlled CO₂ conditions, as a function of time and distance along the flow path within the column. The HPCFR is more advanced than standard reactor experiments which are usually performed in tens to hundreds of ml reactors, and it simulates more closely the real field scale injection. The column experiments can be carried out under high pressure and elevated temperature together with in-line monitoring of vital parameters necessary to predict the progress of H₂O–CO₂–basalt interaction such as total dissolved inorganic carbon (DIC) and pH. In addition, samples of solute are taken on different horizons along the flow path within the column. After the experiment is finished, solid samples

between different compartments along the flow path can be analysed to complement the solute chemistry analyses. Chemical data obtained from the experiment can be used in reactive transport models to elucidate the advance of reaction fronts, forecast porosity changes and estimate the upper limit for CO₂ injected into a given geological formation.

A conceptual model of CO₂ injection into natural basaltic formation and into the column filled with basaltic glass grains is similar. In the beginning of the flow path, dissolution is predicted to be the dominant process due to low pH of the CO₂-charged fluid, but with distance secondary carbonates are expected to form (Fig. 1).

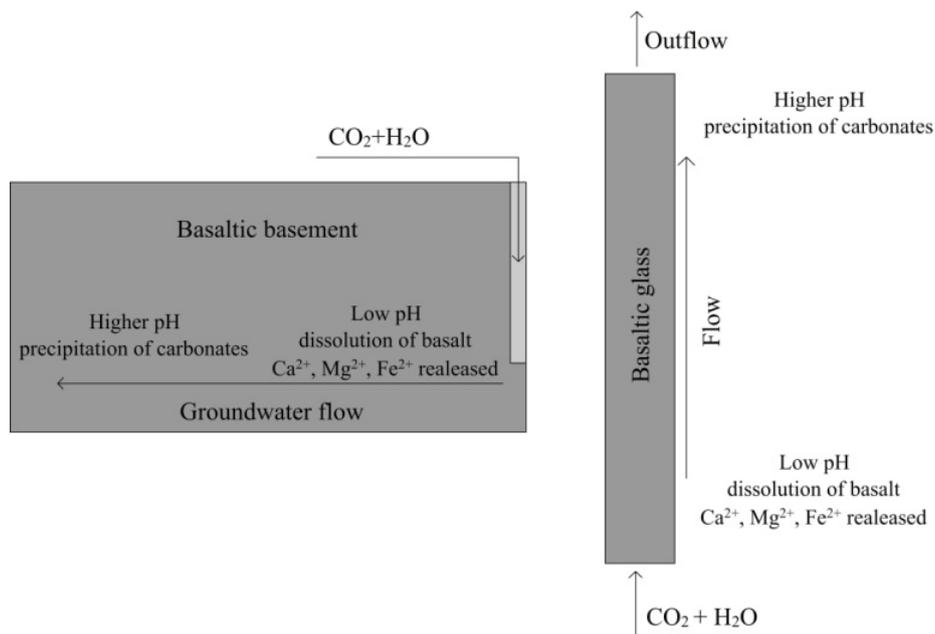


Figure 1. A conceptual model of CO₂ fixation during the field scale CarbFix project (left) and during the column flow experiment (right). In both cases, it is anticipated that in the beginning of basalt–H₂O–CO₂ interaction dissolution of rocks will be the dominant process whereas at later stages, as a result of proton consumption by basalt dissolution, pH will increase resulting in carbonates precipitation.

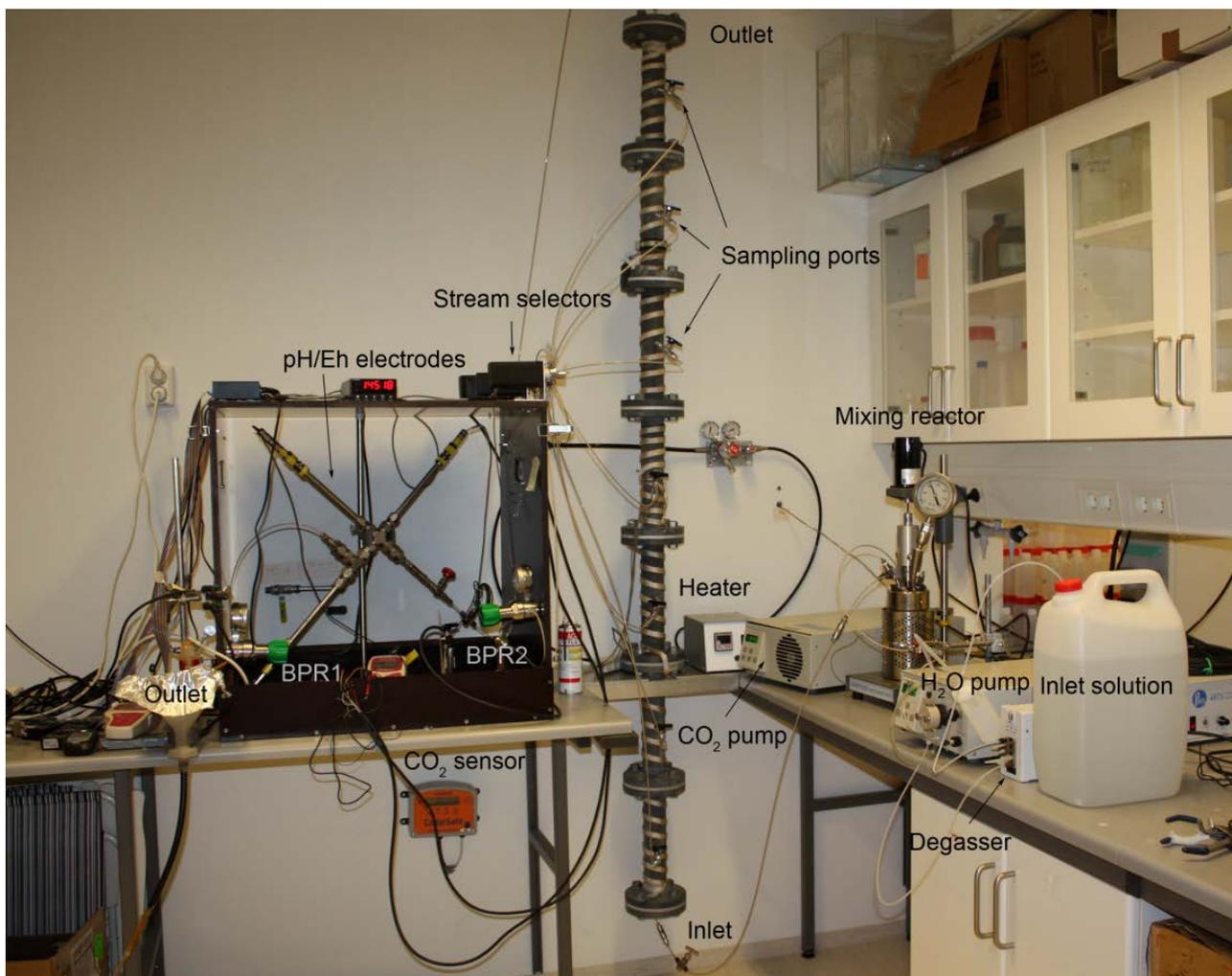


Figure 2. The experimental design. The CO₂-H₂O mixture is pumped through the mixing reactor into the column. From the column the reactive fluid passes a stream selectors where it is directed through pH/Eh electrodes and towards the back pressure regulator (BPR1) and finally to the outlet.

Full description of the experimental design of the HPCFR is provided in Galeczka et al., 2013a. The photograph of the experimental design with major components of the set-up is presented in Fig. 2. The short and long term CO₂-charged fluid injections into the column were carried out in the past and results of the fluid analyses are explored in Galeczka et al., 2013b and Galeczka et al., 2014. The CO₂-charged fluid experiments carried out in the column do not only mimic the CO₂ injection and storage but they also reflect the natural processes of CO₂ fixation in volcanic terrains. Another example of natural CO₂ storage, apart from weathering of silicates, is the fixation of CO₂ released from magmatic intrusions into groundwater, surface waters and glacier melt waters.

Short description of the experimental design

The experimental set-up consists of 7 titanium compartments assembled into a 2.5 m long vertical pipe, with 5.8 cm outer and 5 cm inner diameter, corresponding to a volume of ~ 5 dm³. During the past experiments, column was filled with 45 to 100 μm basaltic glass grains, of known chemical

composition and surface characteristics. Liquid carbon dioxide was mixed with DI water at certain ratio to assure full dissolution of CO₂ in the water and pumped under 80 bar of hydrostatic pressure through the column. An 8-port multi-position stream selector connected to each compartment of the column enabled sampling of the evolving fluid chemistry along the column. During the sampling process, the reactive fluid flowed through a sampling loop of specified volume, followed by in-line pH and Eh electrode cross. An expander that was connected to the sampling loop measured dissolved inorganic carbon. After the experiment was finished samples of solid material were taken from all intervals of the plug and initially examined by SEM-EDS.

Results of experiments – water chemistry

During the pure water-basaltic glass interaction experiment, the pH of the injected water evolved rapidly from 6.7 to 9–9.5 and most of the dissolved iron was consumed by secondary mineral formation, similar to natural basaltic groundwater systems. The reactive fluid was undersaturated with respect to basaltic glass and carbonate minerals, but supersaturated with respect to zeolites, clays, and Fe hydroxides.

Basaltic glass dissolution in the CO₂-charged water was closer to stoichiometry than in pure water. The mobility of metals increased significantly in the reactive fluid and the concentration of some metals, including Mn, Fe, Cr, Al, and As exceeded the WHO (World Health Organisation) allowable drinking water limits. Iron was mobile and the aqueous Fe²⁺/Fe³⁺ ratio increased along the flow path. The pH rose only from an initial pH of 3.4 to 4.5 along the first 18.5 cm of the column, and then remained constant during the remaining 2.1 meters of the flow path.

Increasing the temperature of the CO₂-charged fluid from 22 to 50 °C increased the relative amount of dissolved divalent iron along the flow path. After a significant initial increase along the first metre of the column, the dissolved aluminium concentration decreased consistent with its incorporation into secondary minerals. The dissolved chromium concentration evolution mimicked that of Al at 50 °C, suggesting substitution of trivalent Cr for Al in secondary phases. According to PHREEQC calculations, the CO₂-charged fluid was always undersaturated with respect to carbonate minerals within the column, but supersaturated with respect to clays and Fe hydroxides at 22 °C and with respect to clays and Al hydroxides at 50 °C.

Results of experiments – solid chemistry

To complement the results of solute analyses of the reactor's initial pure water- and CO₂-charged water-basaltic glass interaction experiments, solid samples from the seven compartments along the flow path within the column were analysed with Scanning Electron Microscopy Energy dispersive X-ray spectroscopy (SEM/EDX). After the CO₂ experiments were finished, the DI water was pumped through the column to avoid solidification of the basaltic glass and minimize precipitation of the secondary minerals. Disassembling of the column started by disconnecting the flanges from the top compartments and continued downwards. Each compartment was removed separately and 316 stainless steel SS tray was used to keep material inside the column during disassembling. Several uppermost centimetres of consolidated material were removed from the compartments

using SS spoon and SS trace, and the rest using hydraulic press. The material from each compartment (Fig. 3) was divided into several sets and cleaned separately by repeated rinsing with DI water (Fig. 4). This cleaned material was dried in the oven in 60 °C for several days.



Figure 3. The appearance of the basaltic material glass in the first compartment after unscrewing the column reactor.



Figure 4. Dividing and cleaning the solid samples.

Macroscopic observations indicate light brown concentric alteration products at the inlet of the first compartment, indicating fast fluid–basaltic glass interaction at the initial reaction front. The concentric alteration continues for several centimetres up with the flow direction. There is no visual change of basaltic glass surfaces throughout upper compartments. Preliminary SEM examination indicates that pitting, etching and various alteration products are present on the basaltic glass surfaces, with the most affected material in the first three compartments (Fig. 5). A lesser degree of alteration of the grains was observed in the last four compartments, with many grains seemingly unaffected. Initial chemical composition of altered versus unaltered basaltic glass grains suggest an overall decrease in SiO_2 , and Na_2O , and an increase in TiO_2 , FeO and Al_2O_3 .

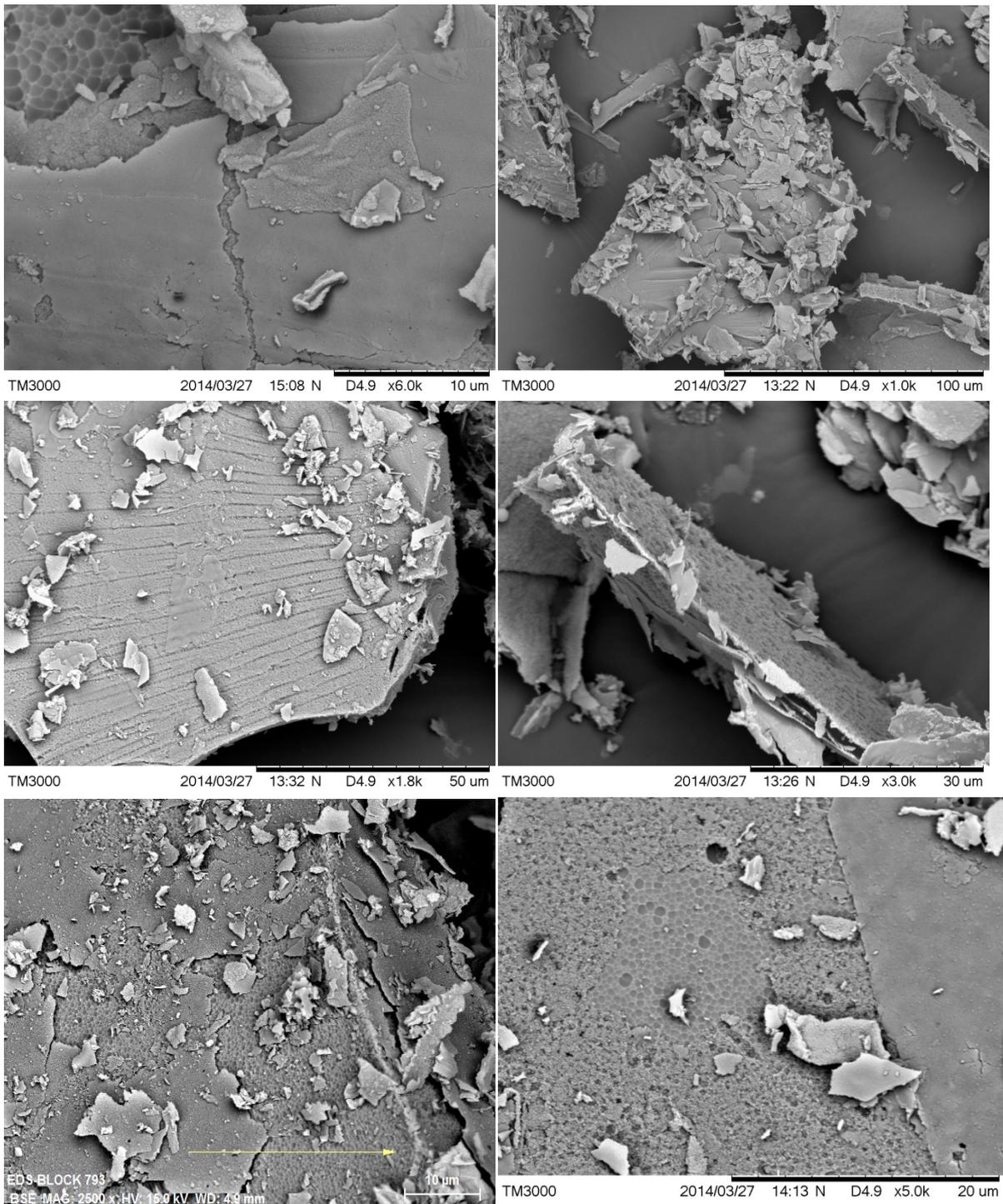


Figure 5. The SEM microphotographs of altered material from the first compartment.

There is no gradual change in elemental concentrations along the flow path inside the column. For example the highest average Fe and Mg concentration comparing to reference material was measured in compartment 6, Ca in compartment 1, and Al in compartment 4. The lowest average Si and Na concentration comparing to reference material was observed in compartment 6. Further investigation has to be performed to determine which phases could have precipitated during each

experimental run. To do this, water and solid chemical composition, modelling results, and natural analogues will be compared.

Current experiments

Current and future experiments using setup described above will be modified with a SFT-10 CO₂ syringe pump (Supercritical Fluid Technologies); this provides slower flow rates and increases residence times of the fluid within the column, thereby enabling longer water-rock interaction before the fluid exits the column. As a result pH will increase and therefore precipitation of secondary phases will be favoured. It is expected that the fluid within the column will become neutral in contrast to previous experiments where pH was buffered at pH 4.5. Characterization and quantification of these secondary minerals (carbonates and clays) are crucial to forecast porosity changes and to estimate upper CO₂ limits injected into a given geological formation.

According to the manufactures specifications for the high pressure liquid chromatography water pump (HPLC) and syringe CO₂ pump, the total flow rate of the fluid through the column could be decreased from 3.63 ml/min used in the previous CO₂ experiments to 0.055 ml/min which will correspond to the residence time of 27 days. According to preliminary reaction transport modelling, if the total flow rate of the ~ 1M CO₂-charged fluid is slowed to ~1.6 ml/min, the reaction fluid will be supersaturated with respect to carbonate minerals (dolomite, siderite). This indicates that the residence time of the fluid inside the column is crucial to approach conditions favourable for secondary phases precipitation.

Preparation of the experimental set-up for current and future experiments has been accomplished and it included:

1. Polishing and heating up the column compartments to remove alteration products from previous experiments and strengthen the corrosion resistance of titanium.
2. Acid washing of the titanium and Hastelloy filter bodies and frits and rinsing it thoroughly using pure DI water.
3. Preparation and testing of the high pressure pH and Eh electrodes.
4. Testing of the actual HPLC pump flow rates to estimate the lowest residence time of the fluid within the column.
5. Grinding and sieving of the Stapafell basaltic glass.

The new SFT-10 pump will be initially tested using pure liquid CO₂ at whereas various gas mixtures would be considered in later stages of the experiments. The aim of these experiments is to assess the risk of toxic metal mobility during the CO₂-charged water pulses into the basaltic rocks.

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