

GHGT-10

CO₂ sequestration in basaltic rocks in Iceland: Development of a piston-type downhole sampler for CO₂ rich fluids and tracers

H. A. Alfredsson^{1*}, D. Wolff-Boenisch, and A. Stefánsson

Institute of Earth Sciences, University of Iceland, Askja, Sturlugata 7, Reykjavík 101, Iceland

Abstract

The reduction of atmospheric CO₂ is one of the challenges that scientists face today. University of Iceland, Reykjavik Energy, CNRS in Toulouse and Columbia University have started a cooperative project called CarbFix (www.carbfix.com) aiming at CO₂ mineral sequestration into basalts at Hellisheidi, SW Iceland. Gaseous CO₂ will be injected into a borehole where it will be carbonated with Icelandic groundwater. The CO₂ charged injection fluid will be released into the target aquifer at ca. 500 m depth at about 35°C and 40 bar. The aim is to permanently bind CO₂ into carbonates upon water-rock interaction. In order to evaluate the hydro-geochemical patterns and proportions of CO₂ mineralization in the aquifer, full scale monitoring is needed. This will involve monitoring of conservative and gas tracers injected with the carbonated fluid, isotope ratios and major and trace elemental chemistry. A crucial issue of the monitoring is the quality of the sampling at depth and under pressure. Commonly, gas bubbles are observed when using commercial downhole samplers (bailers) and in order to avoid this problem, a piston-type downhole bailer was designed, constructed and tested as part of the project.

© 2011 Published by Elsevier Ltd.

Keywords: CO₂ sequestration; mineral carbonation; downhole sampling; bailer; geochemical monitoring

1. Introduction

The reduction of industrial CO₂ emissions is one of many challenges that scientists face today [1-4]. Storage of CO₂ as solid Ca, Mg and Fe carbonates in basaltic rocks may provide a long lasting and thermodynamically stable solution [5]. University of Iceland, Reykjavik Energy, CNRS in Toulouse and Columbia University have started a cooperative project called CarbFix (www.carbfix.com) aiming at CO₂ mineral sequestration into basalts. The targeted field site for the injection of CO₂-charged water is the Hellisheidi area in SW-Iceland [6].

The overall aim of the project is to mineralize CO₂ in the form of solid carbonates by interaction of CO₂ charged water with basaltic rocks [5]. The injection borehole, HN-2, is approximately 2000 m deep and cased down to 400 m. It is planned to inject gaseous CO₂ together with groundwater provided from an adjacent deep groundwater well into the borehole where it has been demonstrated that CO₂ will be fully carbonated before entering the aquifer at ~500 m depth [7]. In order to evaluate the hydro-geochemical patterns and proportions of CO₂ mineralization in the

* Corresponding author. Tel.: +354 525 5248.

E-mail address: haa4@hi.is.

aquifer, a full-scale monitoring program is required. It includes monitoring of conservative, gas and isotope tracers injected with the waters, amidorhodamine G (acid red dye) and trifluoromethylsulphur pentafluoride (SF_5CF_3) as well as the water composition. This requires high quality sampling at depth and under pressure. Commonly, gas bubbles are observed when using commercial downhole samplers (bailers), which is not suitable for sampling of CO_2 -charged waters. In order to quantitatively describe the CO_2 - H_2O system under injection conditions, two out of the six crucial parameters pH, $f\text{CO}_2$, alkalinity, HCO_3^- , CO_3^{2-} , and DIC have to be determined with utmost accuracy. Therefore gas bubbles in the bailer have to be suppressed as much as possible and consequently, a new piston-type downhole bailer was designed, constructed and tested in order to be deployed during the upcoming phase of CO_2 injection at the Hellisheidi site.

2. Piston-type bailer

The bailer is a 160 cm long, 40 mm x 30 mm (ODxID) stainless steel pipe, corresponding to a sampling volume of ~1 L (Fig. 1A). It withstands pressures of ≤ 100 bar and temperatures expected at injection depth ($\leq 50^\circ\text{C}$). Removable threaded caps are located on both ends of the bailer (Fig. 1, box 1 and 4) to open the bailer and remove/replace the piston and clean the interior of the bailer, if needed. The caps have a 5 mm diverted sampling-hole, placed in the middle of the internal side, connected with a $\frac{1}{4}$ " threaded female connection on the surface of the cap. Swagelok™ ball and adjustable check valves are connected to the caps, controlling the inlet and outlet flow (Fig. 1B). This asymmetric set-up was mandatory as the diameter of the sampling pipe in the borehole is only 50 mm meaning that the distance from valve handle to its bottom cannot surpass this limit.

The key component of the piston-type bailer and new feature hitherto not found in commercially available ones, is a movable internal Teflon piston of 10 cm length with four U-rings on its extreme ends (Fig. 1, box 3). This allows the application of an external hydrostatic pressure on the sampled fluid that forces bubbles that may have potentially formed during the sampling process back into the fluid. Note that the cap on the sampling end has therefore a cone-shaped inner side to concentrate these potential bubbles. The piston is also used to pump out the sample for further treatment and analysis. Additionally, besides the inlet check valve (CV) a second CV is installed at the outlet to maintain the flow of DI water out of the bailer (Fig. 1 and 2). A capillary tube, working as a flow restrictor (Fig. 1B) controls the sampling speed. The outlet is connected to a tube to the surface.

On top of the end caps, removable protection caps are installed to avoid damage during the downhole sampling (Fig. 1B, box 5).

3. Sampling procedure

First, the sampling compartment of the bailer (<5mL) is filled with bubble-free and degassed DI water. On the upper side of the piston, the bailer is then entirely filled and pressurized with 1L of DI water up to 30 bar. The outlet CV has been adjusted to hold 30 bars. Thus, the pressure gradient extant between outer pressure during sampling (ca. 40 bar), and inlet and outlet CV (ca. 35 bar, as piston adds some back pressure) will enable a relatively smooth inflow of carbonated and reacted fluid. A flow restrictor is also needed to adjust the sampling time in order to minimize any CO_2 degassing when the inlet CV burst open for sampling.

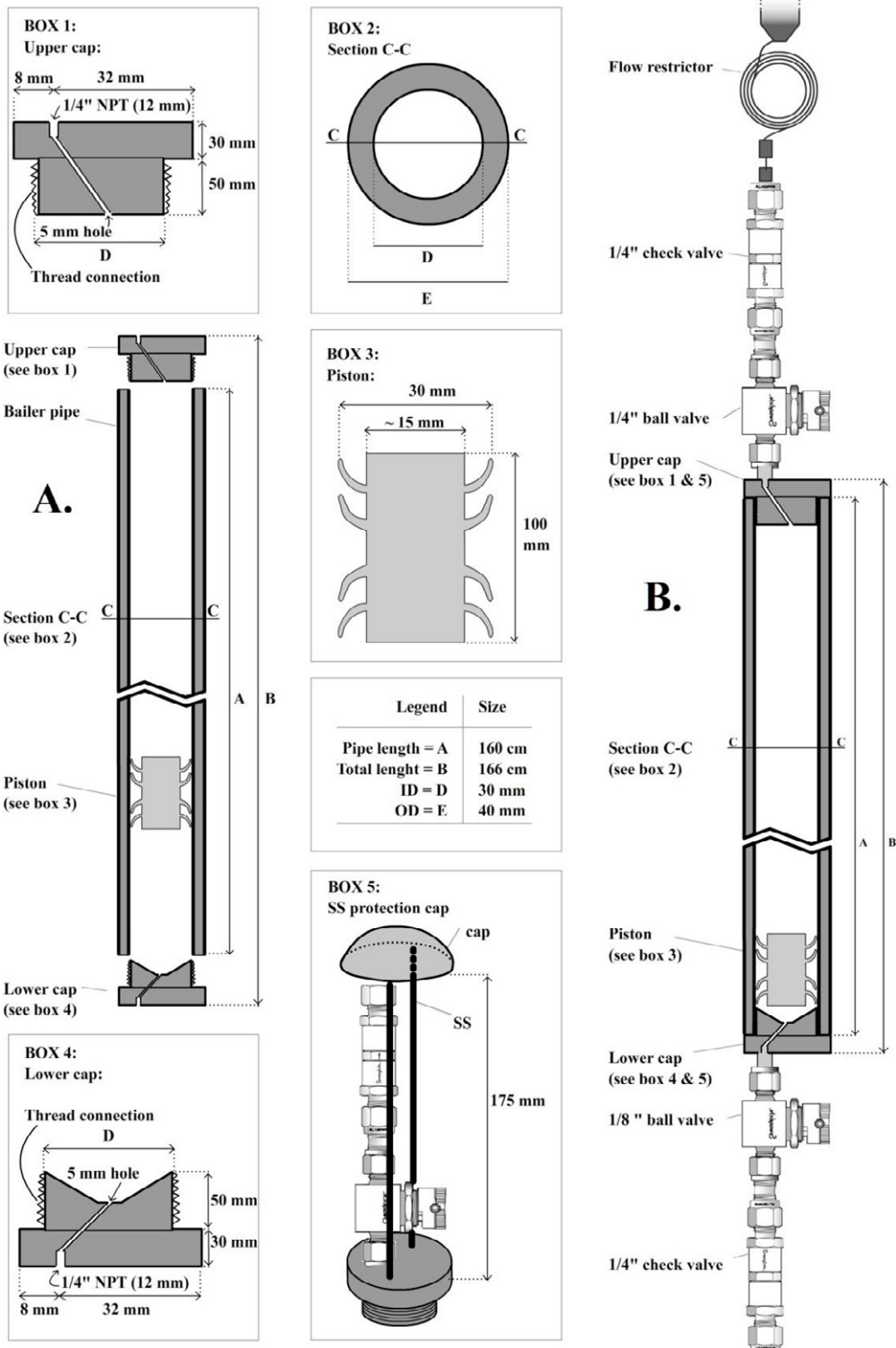


Figure 1 A) Basic construction of the piston-type bailer. Illustrations of the upper cap can be shown in box 1, a section of the pipe in box 2, the piston in box 3 and the lower cap in the box 4. B) The bailer setup for downhole sampling. Ball- and check valves are connected to the upper- and lower caps, for sampling control. A flow restrictor controls the sampling speed and is connected to a tube to the surface. Stainless steel protection caps are placed on the both extremes (box 5).

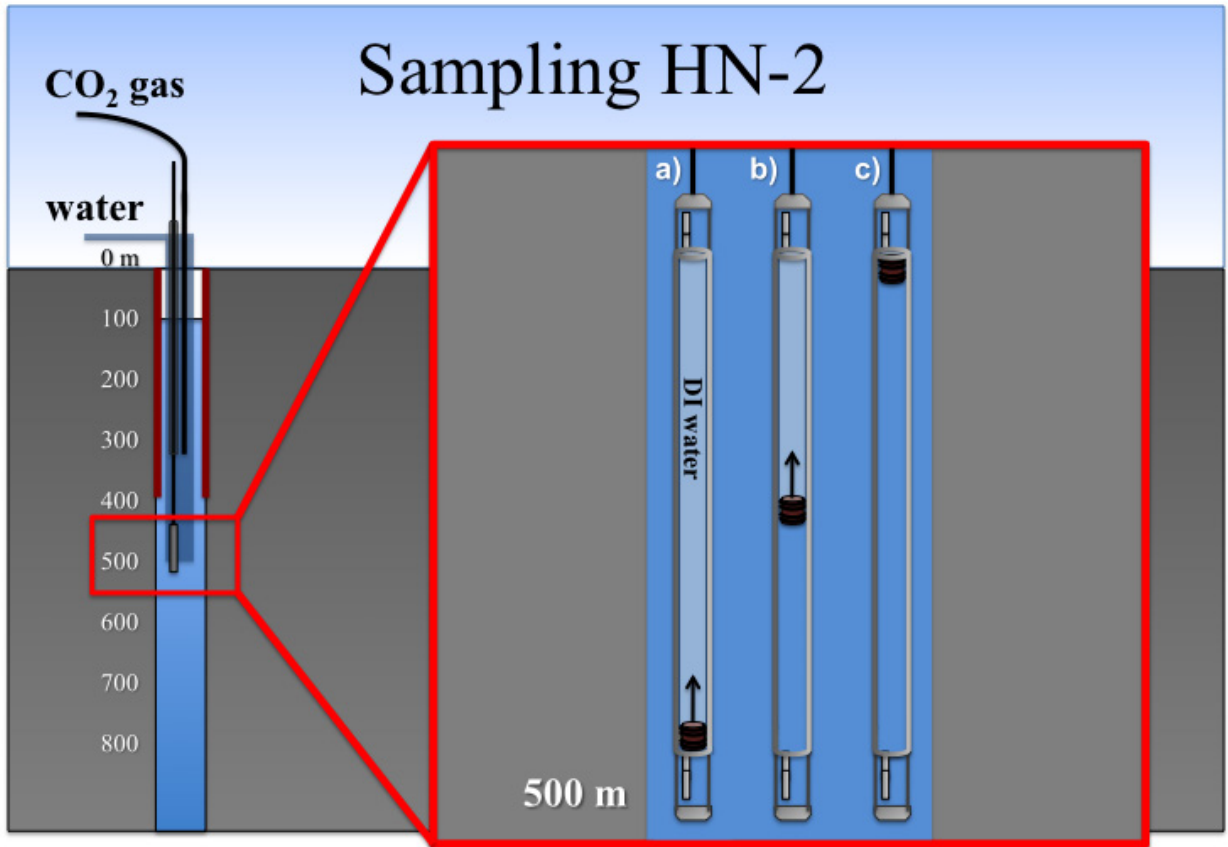


Figure 2 An example of a downhole sampling at 500 m depth in the CO₂ injection well HN-2. The bailer is lowered through a sampling pipe down to 300 m depth, where the CO₂ gas mixes with the injected water. When the bailer reaches 500 m depth, a) The CV opens and the CO₂ loaded waters start to flow into the sampling end of the pipe, moving the piston upwards and squeezing the DI-water out through the upper end. b) The sampling is half way through after ~1 hour and c) sampling is finished in about two hours time.

The bailer is then lowered into HN-2, through a 50 mm sampling pipe down to 350 m and further down to 500 m where the carbonated injection fluid is released into the aquifer (Fig. 2). The sampling end goes first in the borehole, and the bailer is sampled bottom-up. When the bailer reaches 500 m depth, the outer pressure causes the CV to open and sampling takes place (Fig. 2).

The flow restrictor on the outlet (adjusted for approximately two hours sampling) enables the runoff of the DI water which enters a tube connected to the surface of the well.

Once the bailer has been hauled to the surface it is hooked up to a specially designed sampling line (Fig. 3). By pumping DI water into the upper side of the piston a hydrostatic pressure is applied and the bailer is rotated several times for 1-2 hours to force bubbles back into the fluid (Fig. 4). Then the sampling equipment is connected to the bailer and the CO₂ water sample passes through a sampling loop (of known size) and exits via a backpressure regulator. In situ measurements of pH and pE are performed by high P/T electrodes (Corr Instruments, TX) placed in-line (Fig. 3A).

The sampling loop is used to get a known sample volume for determination of the DIC. The CO₂ is degassed out of the loop into a syringe containing a strong base to collect all CO₂ for subsequent titration analysis (Fig. 3B). For dissolved elements, fluid is simply collected after depressurization.

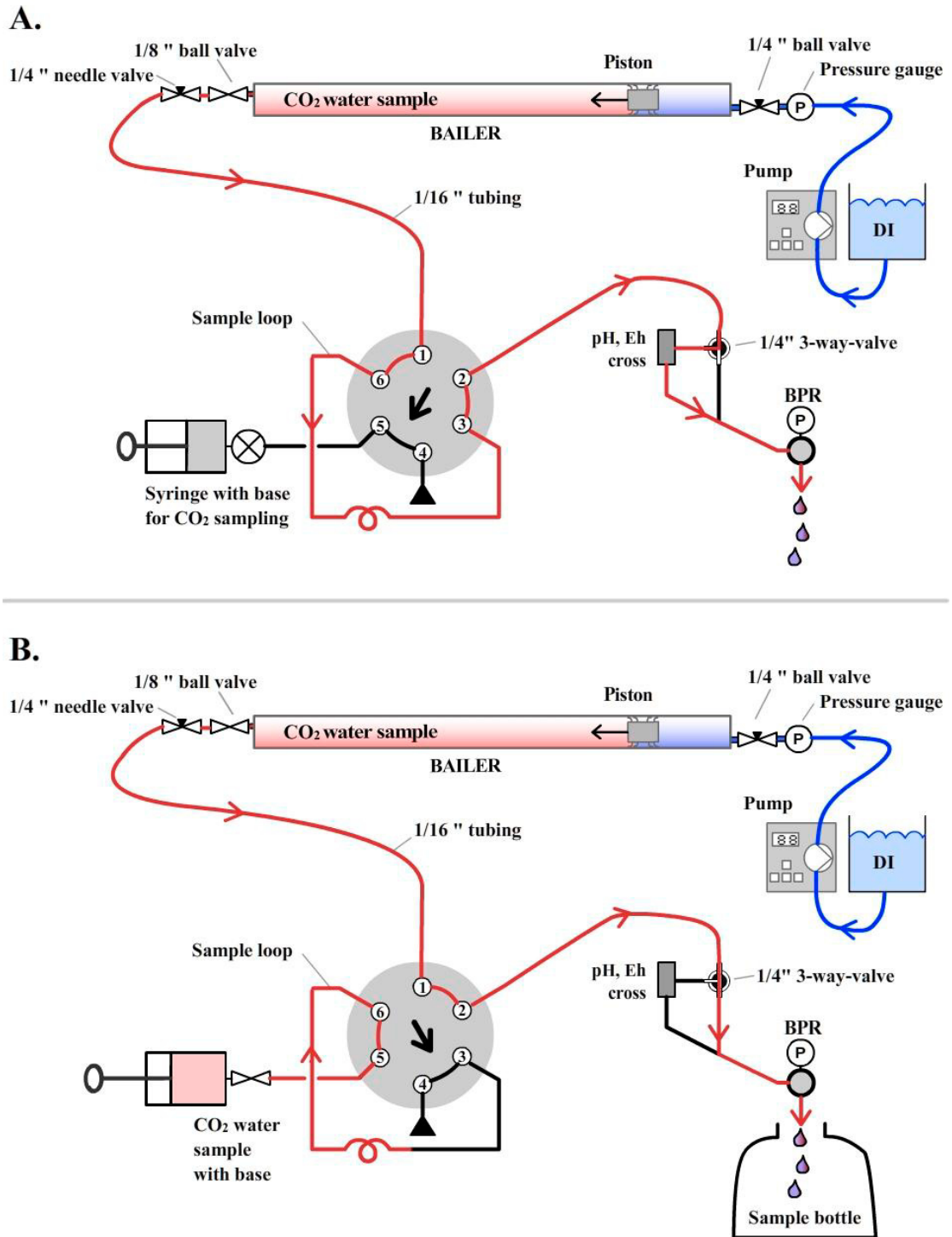


Figure 3 Setup for the on-site sampling of the bailer. A high pressure piston pump is added to the upper side of the piston (on the right) with a pressure gauge. The sampling line consists of a 1/4" needle valve, a 6 port – 2 way valve with a 0.79 mL sample loop, a syringe for CO₂ sampling, in-line P/T electrodes for pH and Eh followed by a back-pressure regulator (BPR). A) Filling of the sample loop and simultaneous pH/ pE determination. B) Gas expansion from the sampling loop into a syringe, containing KOH for CO₂ collection and analysis; dissolved metals are now sampled after exiting the BPR.

When depressurizing the sampling loop the released CO₂ gas is quantitatively collected in a 0.5 molar KOH solution where all CO₂ converts into carbonate according to:



For two moles of reacted KOH one mole of CO₃²⁻ is produced. There are different analytical ways of determining the initial dissolved inorganic carbon (DIC) present at injection depth and therefore in the bailer (e.g., titrimetry or ion chromatography [8]). Yet, another much faster and more convenient way (especially in the field) is by repeated pH measurements (so-called standard addition technique). A special wide pH-range electrode (Eutech InstrumentsTM CyberScan pH 110) records the change in pH as a function of the sampled volume. Delta pH is then recalculated to the amount of consumed OH moles and this value plotted against the sampling volume. In order to obtain different volumes, the sampling loop is degassed repeatedly into the same base and the change in pH recorded after each step. The slope of such a linear plot yields the concentration of consumed OH- in Eqn. (1), and by extension the desired molar carbonate concentration. This approach may seem less accurate than titrimetric or chromatographic methods in that it is limited by the precision of a glass electrode but concentrations are, after all, extracted from a linear regression of multiple data points which offsets this limitation and produces values whose relative standard deviations are on the order of 4%, quite comparable to more sophisticated techniques. This method is also the preferred choice at the injection site as DIC concentrations in the injection well will lie around 1 mol/L and this would call for heavy dilution (with inherent errors) before titration or injection onto an IC column. However, this technique works strictly only if no sample fluid enters the base upon degassing of the sampling loop. Otherwise, dilution as well as silicic acid and other cations present in the sample will change the concentration of free hydroxyls in the base and therefore may cause an inaccurate reading (depending on the sampling volume and solute concentrations relative to those of the base). Carry-over of ca. 60% sampling fluid from the loop into the base could not be averted (ca. 500 µL). However, comparing this volume with a KOH base of 50 mL and even assuming a 100fold increase in TDS compared to background values found presently in injection waters yields only a 1% error on the DIC determination.

4. Laboratory tests

Lab tests under injection conditions provided the information on the adjustment of the CV's cracking pressures to create a low-pressure gradient between the bailer system and the outer pressure. Thus, at sampling pressure (ca. 40 bar), the combined lower pressure between inlet and outlet CV (ca. 35 bar) will enable a relatively smooth inflow of CO₂ dissolved fluid. The check valves open fully at the cracking pressures, so a flow restrictor is needed to adjust the sampling time. By adjusting the time to two hours, degassing can be minimized down to several milliliters during sampling.

Degassing cannot be averted totally but the piston ensures that most of the CO₂ and concomitant amounts of tracers can be dissolved back into the fluid. The bailer was connected to a 5L batch reactor, containing CO₂ saturated water at 40 bar. During these lab-tests, the bailer was filled with carbonated water from the batch reactor and connected to a glass tube setup (Fig 4). DI water was used to over-pressurize the sampled fluid, and the bailer was rotated several times for 1 – 2 hours. The sample end was connected to an in-line glass tube, under pressure, controlled by a back pressure regulator. So if there was a gas bubble in the system, it was detected and measured through the glass during the release of the CO₂-water sample.

The main results from the tests are that gas bubbles created during sampling are nearly impossible to avoid. By over-pressurizing the bailer for ~ 2 hours after sampling, most of the gas is dissolved back into the fluid. After numerous tests, bubbles were varying from 0 – 9 vol. % of the total bailer volume. (Tab. 1)

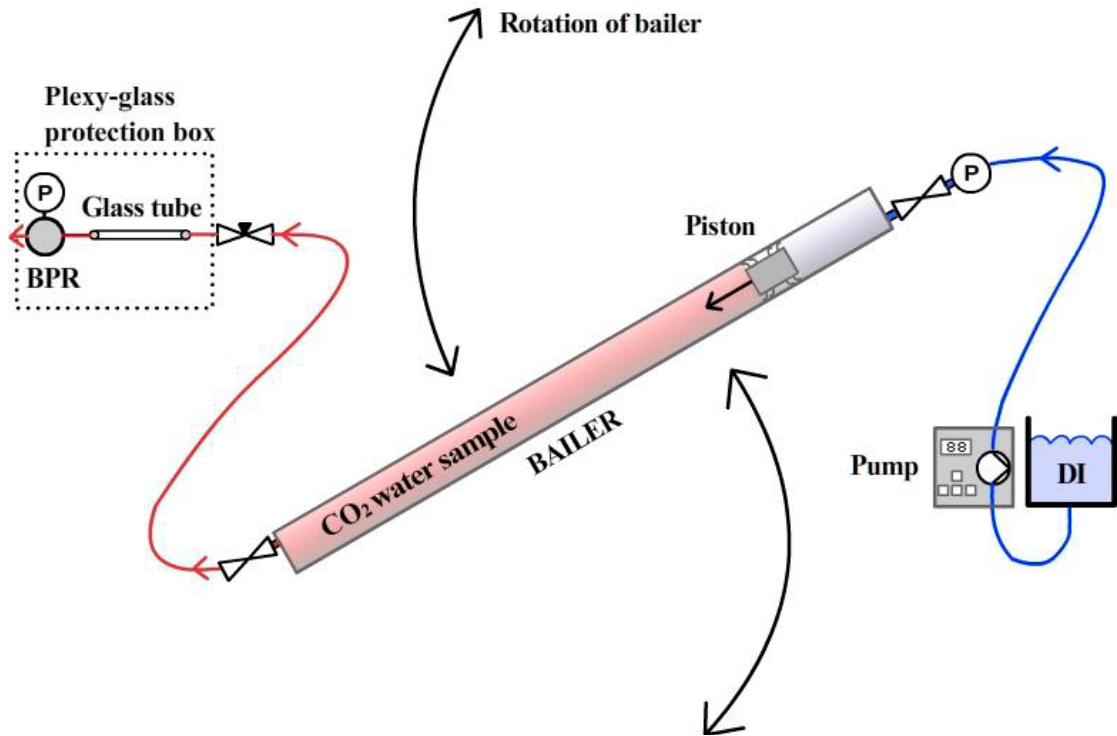


Figure 4 The glass tube setup. A glass tube is inserted between a needle valve and the back pressure regulator (BPR) for determining any gas-bubbles in the CO₂ water sample. A high pressure piston pump is connected to the upper piston side and controls the pressure and flow-through rates.

Table 1 Lab tests under various setups and sampling time.

Test	Setup*	Pressure	Sampling time	Sample size	Over pressure	Over pressure time	Bubble size
		bar	hour	mL	bar	hour	mL
1.	T-NV-BV-B-BV-CV(24)	44	2.20	1012.5	70	1.5	0
2.	T-NV-BV-B-BV-CV(24)	44	0.05	914.6	70	1.5	8
3.	T-P-CV-BV-B-BV-CV-FR	43	2.85	1035.5	70	1.6	0
4.	T-P-CV-BV-B-BV-CV-FR	43	2.83	995	80	1.5	9
5.	T-P-CV-BV-B-BV-CV-FR	43	2.66	985	80	2.5	3.3

*T = tank of CO₂ water at 40 bars; B = bailer; CV(24) = check valve (cracking pressure); NV = needle valve; BV = ball valve; FR = flow restrictor

5. Conclusions

The bailer is well designed to sample pressurized carbonated fluids and a specially designed sampling line enables the measurements of the vital parameters DIC and in situ pH, besides the redox state.

Degassing cannot be totally averted during sampling but the piston ensures that nearly all of the CO₂ (>99%) is re-dissolves in the fluid. The remaining volume of gaseous CO₂ is very small and will not tangibly effect the quality and accuracy of the data. Note that in two cases no bubbles were found at all after the piston treatment and this suggests that with more testing and adjustments of the amount of time and pressure that is applied on the piston this new bailer could eventually be deployed to determine also volatile and relatively insoluble tracers that inevitably

accumulate in the gas phase. Altogether, this bailer gives us confidence in acquiring quality samples for major and trace elemental analyses, including isotope ratios and conservative tracers injected with the fluid.

Acknowledgements

We would like to thank Sigurður Reynir Gíslason at the University of Iceland, Hólmfríður Sigurðardóttir and Bergur Sigfússon at Reykjavík Energy, Eric H. Oelkers from CNRS - Toulouse, Martin Stute and Juerg M. Matter from Columbia University, for insightful discussions during the development and construction of the bailer. Þorsteinn Jónsson at the University of Iceland is especially acknowledged for his technical contribution. We are also indebted to Eydís S. Eiríksdóttir, Iwona M. Galezka, Kiflom G. Mesfin, Snorri Guðbrandsson, Alex P. Gysi and Gabrielle J. Stockmann at the University of Iceland for their help and great support. Finally, we thank Júlía K. Björke at the University of Iceland for her endless patience during this study. This project was financed by Reykjavík Energy and its Environmental and Energy Research Fund.

References

- [1] Broecker WS. Climate change: CO₂ arithmetic. *Science* 2007; 315: 1371.
- [2] Broecker WS. CO₂ capture and storage: possibilities and perspectives. *Elements* 2008; 4: 295-7.
- [3] Oelkers EH, Cole DR. Carbon dioxide sequestration. A solution to a global problem. *Elements* 2008; 4: 305-10.
- [4] Metz B, Davidson O, de Coninck H, Loos M, Meyer L (Eds.). IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, New York; 2005.
- [5] Gíslason SR, Wolff-Boenisch D, Stefánsson A, Oelkers EH, Gunnlaugsson E, Sigurðardóttir H, *et al.* Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *Inter J Greenhouse Gas Control* 2010; 4: 537-545.
- [6] Alfredsson HA, Hardarson BS, Franzson H, Gíslason SR. CO₂ sequestration in basaltic rock at the Hellisheidi site in SW-Iceland: stratigraphy and chemical composition of the rocks at the injection site. *Min. Mag* 2008; 72: 1-5.
- [7] Alfredsson HA, Gíslason SR. CarbFix – CO₂ sequestration in basaltic rock: chemistry of the rocks and waters at the injection site, Hellisheidi, SW-Iceland. *Geochim Cosmochim Acta* 2009; 73: A28.
- [8] Arnórsson S, D'Amore F, Gerardo-Abaya J. Isotopic and Geochemical Techniques in Geothermal Exploration, Development and Use: Sampling Methods, Data Handling, Interpretation (ed. Arnórsson S), International Atomic Energy Agency Publication, Vienna; 2000.