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Experimental studies of basalt-H_2O-CO_2 interaction with a high pressure column flow reactor: the mobility of metals

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Abstract

Here, we report on the mobility of metals at the early stage of CO_2 injection into basalt, before significant precipitation of secondary minerals. Short-lived pulses (50-100 hours) of CO_2-charged water were injected into a high pressure column flow reactor filled with basaltic glass grains at 22°C, 8 MPa of total pressure and a velocity of 0.4 cm/min. The residence time of the water within the column ranged from 8 to 10 hours. The column was conditioned with pure water, resulting in alkaline outflow (pH ~9). The pH of the inlet CO_2-charged water was ~3.2, and the lowest pH measured in the column was 4.5, after less than 10 hours of water/rock interaction. The dissolved metal concentrations and metals relative mobility increased dramatically during the CO_2-pulses; more than 100 times for Sr, Fe, Al, Ca, Ba, Mn, and Mg. Of these elements, all but Al can bind with CO_2 to form carbonate minerals. Only the dissolved Al, Fe, Mn and Cr concentrations exceeded allowable drinking water limits. After the CO_2-pulses, all of the elemental concentrations decreased close-to or even below what was measured during the conditioning of the column. The pH never reached ~9 which was the initial pH before CO_2-pulses.
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1. Introduction

The safest way of carbon sequestration is mineral carbonatization, when CO_2 is fixed as stable carbonate minerals [1, 2]. Mineral storage requires combining CO_2 with divalent cations such as Ca^{+2}, Mg^{+2} and Fe^{+2} which are the constituents of the host rock. Basalts and ultramafic rocks are the largest and the most efficient sources of these elements on Earth [3]. This is underscored by the fact that despite basalt

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covering less than 10% of the Earth's continental surface its weathering consumes up to 33% of all the CO_2 fixed during weathering of Earth's terrestrial silicates [4]. The oceanic floor covering about 70% of the Earth's surface is mostly made of basalt. The large volumes of mafic (basalt) and ultramafic rocks on the Earth's surface have large CO_2 sequestration capacities. Examples of locations where CO_2 could be injected and allowed to react with the host rock to form carbonates are large igneous provinces, such as the Columbia River basalts, Deccan and Siberian traps, and smaller outcrops of oceanic basaltic crust such as Iceland [1]. The CarbFix CO_2 sequestration pilot project in Iceland [5, 6] has been established to investigate the potential for *in situ* mineral carbon storage in basalt. The injected CO_2-saturated waters are predicted to enhance basalt dissolution, leading to the release of divalent metals into the percolating solution. As a result of proton consumption by basalt dissolution, pH increases followed by carbonate $((Ca,Mg,Fe)CO_3)$ precipitation [1, 3, 5, 6]. Another field project, the Wallula Basalt Sequestration Pilot Project in the USA, was designed to confirm the feasibility of safe sequestration of large quantities of supercritical CO_2 within a deep flood basalt formation [7]. Laboratory studies investigating the efficiency of *in situ* CO_2 storage have mainly focused on the secondary products of the basalt/CO_2-H_2O/CO_2-H_2S/CO_2/$scCO_2$ interaction [8-10]. The basalt, when reacting with the CO_2-charged water, does not only release divalent cations that end up in carbonates, but also releases other metals that can be harmful to biota. The main metals of concern are Al and Cr. Some other elements such as Fe and Mn, for example, can be both essential for life and toxic depending on their concentration. The toxic metal release is the most dangerous at the early stage of injection, when the CO_2-charged water is still at low pH, 3-5, and the metals are mobile. This is before significant precipitation of carbonates, clays, Al- and Fe- oxides and hydroxides that will eventually scavenge the metals [11].

A novel high pressure column flow reactor [12] provides an opportunity to study the relative mobility of metals at the early stage of the CO_2 injection into basalt. In this study we report on the consequences of short-lived (50-100 hours) CO_2-pulses injected into the column filled with basaltic slurry at 22°C and 8 MPa of total pressure. Results of this study will help the understanding of how the basalt-water system responds to sudden changes caused by CO_2 fluxes and how it returns to pH neutrality after the CO_2-pulse ends. The outcome of this experiment is not only applicable to industrial CO_2 storage but also to natural processes such as sudden magmatic CO_2 fluxes into groundwater systems in volcanic terrains such as Iceland [11].

2. Materials and methods

The experiment was carried out in a high pressure column flow reactor (HPCFR) [12]. Liquid CO_2 was mixed with degassed deionized (DI) water and pumped through a vertical column filled with basaltic glass powder. Dissolution and precipitation reactions took place inside the HPCFR and reaction progress was monitored via outlet solute sampling together with pH/Eh measurement (Fig. 1). Basaltic glass used in this study was collected from the Stapafell Mountain located in SW Iceland. The composition of the material is similar to that of mid-ocean ridge basalt (MORB) and its dissolution kinetics was reported in previous studies [13-15]. Its chemical composition is consistent with $Si_{1.0}Ti_{0.024}Al_{0.355}Fe_{0.207}Mg_{0.276}Ca_{0.265}Na_{0.073}K_{0.007}O_{3.381}$. The material was crushed in a jaw crusher and dry sieved to obtain the particle size fraction of 45-100 μm which was subsequently washed by repeated gravitational settling to remove ultrafine particles. The total mass of dry glass particles inside the column was 8.3 kg, the corresponding specific BET surface area equaled 22 000 cm^2/g, while the total surface area amounted to 182,160,000 cm^2. The total mass of aqueous solution, within the column at a given time during the experiment, was 1.84 L assuming 40% porosity, yielding a surface area to solution volume ratio of ~10^5 cm^{-1}.

Due to corrosive nature of CO_2-charged water, nearly the entire reactor was made either of titanium (Ti), Hastelloy® C-276 (HC), or PEEK. The titanium column measures 234×5.8×5.0 cm [L×OD×ID] and holds

a total volume of ~4.6 L. The inlet is placed at the bottom of the vertically aligned column to spread the percolating fluid perpendicular to the flow axis and thus to avoid preferential flow paths via gravitational resistance and lateral spread.

In this study sampling of the solution was done just through the main outlet; however the HPCFR has additionally seven lateral sampling outlets, one in each compartment which can be used to sample the solution along the flow path as it is described in [12]. From the column the solution flowed through a pH and Eh electrode cross (Corr Instruments) where pH and Eh were determined in-line which corresponded to *in situ* pH and Eh. The elevated pressure in the reactor was maintained with a back pressure regulator (BPR, Swagelok®) at the end of the sampling line. The column was wrapped with a heating Tape (HTS/Amptec) keeping the experimental temperature at 22°C ± 1°.

The liquid CO_2 cylinder was placed on a scale and its status was monitored through mass loss. The cylinder was connected to a supercritical fluid pump (Supercritical Fluid Technologies). Degassed DI (deionized water) water was delivered by high pressure liquid chromatography pump, HPLC (Supercritical Fluid Technologies). Both fluids were mixed in a flow-through Ti reactor like the ones routinely employed in mineral dissolution studies [14].
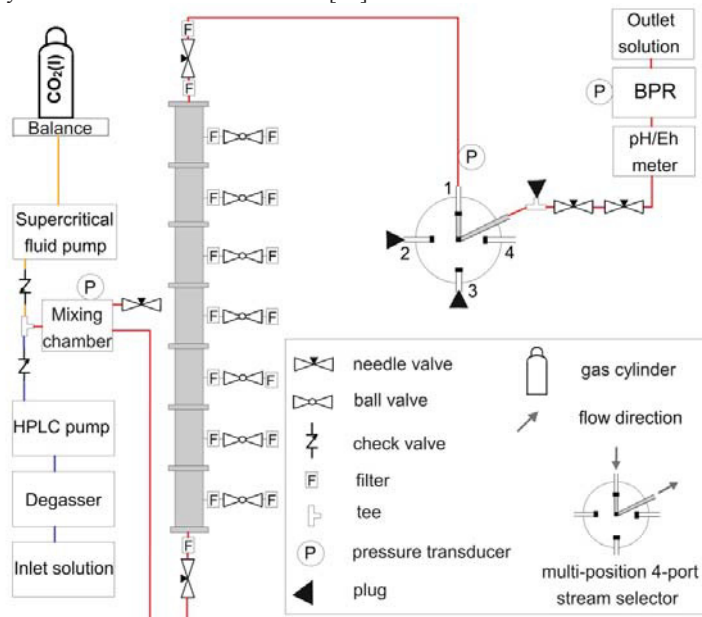

Fig.1. The high pressure column flow reactor (HPCFR). The CO_2 was dissolved in DI water in the mixing chamber and flowed through the column followed by a multi-position 4-port stream selector, and through the pH/Eh cross where pH/Eh was determined in-line. Liquid samples for major and trace elements were eventually collected at ambient pressure from the back pressure regulator (BPR).
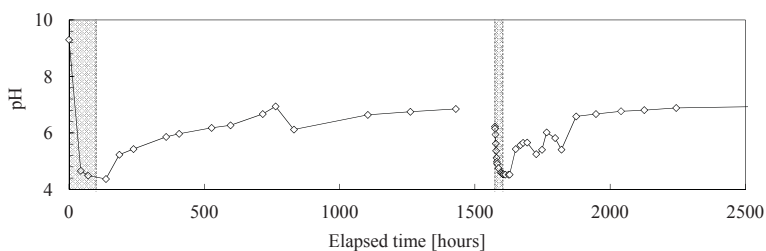
The experiment started with DI water being pumped through the column at 5 ml/min, 22°C and 0.1 MPa for 2500 hours to condition the system. Then, the total/hydraulic pressure was increased to 8 MPa followed by $CO_{2(l)}$ injection. The total pressure and the flow rates of water and liquid CO_2 were set to ensure that the $CO_{2(l)}$ was fully dissolved in the water before entering the column. During the first CO_2-pulse the water was pumped at 3.5 mL/min and $CO_{2(l)}$ at 0.22 mL/min for 100 hours. The residence time of the CO_2-charged water within the column was 8.5 hours. The residence time is calculated by the total
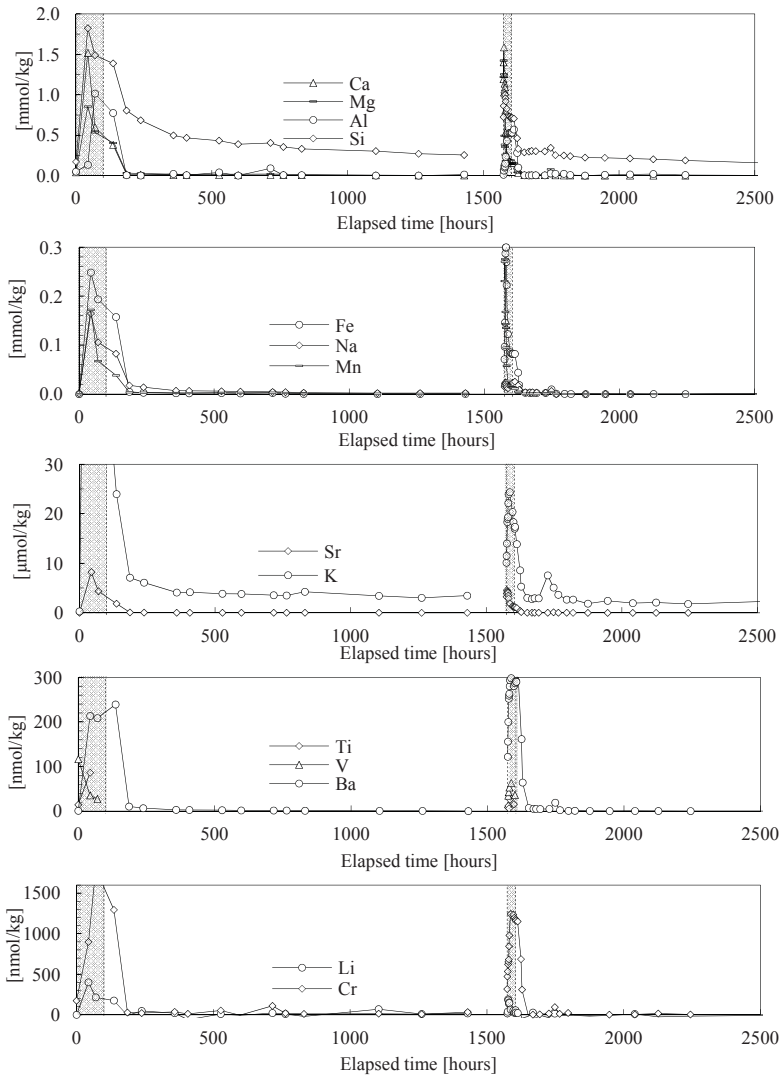
volume of the solution inside the column divided by the sum of the individual pump flow rates. During the second CO_2-pulse water was delivered at 3.0 ml/min and $CO_{2(l)}$ at 0.13 ml/min which corresponds to the residence time of 10 hours. The duration of the second pulse was 50 hours. Initial measured dissolved inorganic carbon (DIC) concentration was ~1.2 mol/L during the first CO_2-pulse and ~0.8 mol/L during the second CO_2-pulse. Based on the initial DIC concentration, the calculated pH of the CO_2-charged water was 3.14 during the first pulse and 3.24 during the second pulse. It took approximately 44 hours (~5 pore volumes) to replace the initial reacted solution of pH~9, which was the result of pure water-basaltic glass interaction, with the CO_2-charged water and to decrease the *in situ* pH to ~4.5. The outlet solution was sampled, filtered using a 0.2 μm cellulose acetate filter, and then acidified with concentrated supra-pure HNO_3 prior to analysis for major elements with Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Analytical uncertainties of ICP-OES analyses are in the order of ≤5%. Selected samples were analyzed for trace elements and rare earth elements (REE) by Inductively Coupled Plasma Quadrupole Mass Spectrometer (ICP-QMS) and/or Sector Field Inductively Coupled Plasma Mass Spectrometer (ICP-SFMS).

The saturation state of the basaltic glass and selected secondary minerals with respect to the solution was determined with the PHREEQC computer code [16] based on the outlet chemical composition, *in situ* pH and Eh. The database used in this study was phreeqc.dat which was updated with Cr thermodynamic properties from llnl.dat and the minerals of interest from [17]. Secondary phases were chosen based on natural analogues and previous experimental work [9, 18, 19]. The dissolved inorganic carbon concentration (DIC) in the outlet was determined by PHREEQC, using the measured chemical composition together with the *in situ* pH and forcing a charge balance. The inlet DIC concentration was measured directly from the mixing chamber with the expander transducer method [12].

3. Results and Discussion

The experiment can be divided into five stages. The first stage corresponds to pure water (DI water) conditioning of the column when DI water was pumped through the reactor. The solute chemistry is represented by the steady-state elemental concentrations of the last samples taken during this stage and it is shown by the first data point on the diagrams in Fig. 2 and 4. The water chemistry at this stage is similar to the chemistry of the groundwater in basaltic terrains which are characterized by high pH 9-10 [20]. The second stage was the first CO_2-pulse, lasting for 100 hours (four days) when the CO_2-charged water entered the system which had been conditioned with DI water during the first stage. During this stage, the *in situ* pH dropped to 4.5 as shown in Fig. 2. In the third stage DI water replaced the CO_2-charged water and the pH rose towards neutrality. The fourth stage is the second CO_2-pulse lasting for 50 hours. This pulse started about two months after the first CO_2-pulse had ended. In the fifth stage DI water replaced the CO_2-charged water. Similar to the third stage, the system returned to its pH neutrality due to the DI water replacement of the CO_2-charged water from the second pulse.
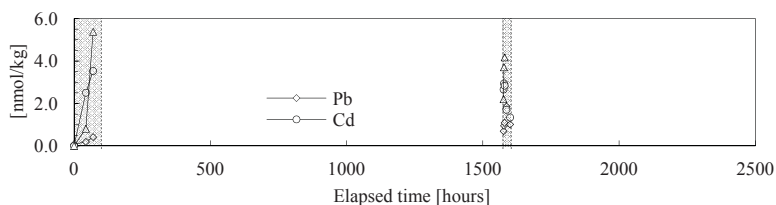
Fig. 2. Results of chemical analyses of samples taken during the five stages of the experiment. First data points in all the plots represent the chemistry of the first stage of the experiment during pure water conditioning of the column. Data points in the shadowed fields correspond to the first and the second CO_2-pulse respectively. All other data points represent the third and fifth stage of the experiment when the system returned to its pH neutrality due to pure water replacement of CO_2-charged water pumped during the CO_2-pulses.

Time series for the pH and selected dissolved elements in the outlet, during the five stages are shown in Fig. 2. The pH decreased rapidly when CO_2-charged water was pumped through the column, resulting in enhanced release of the elements from the rock. The lowest pH measured during both CO_2-pulses was 4.5. The concentrations of all elements increased significantly compared to the concentrations before and after the CO_2-pulses.

The sampling resolution during the second CO_2-pulse allowed assignment of the highest concentrations of the elements to the pH. The highest concentrations of major elements were detected at pH 6.2 for Mg (1.42 mmol/kg); 5.9 for Ca (1.59 mmol/kg), Sr (4.58 µmol/kg) and Mn (275.8 µmol/kg); 5.6 for Si (1.03 mmol/kg) and Na (0.024 mmol/kg); 5.1 for Fe (0.3 mmol/kg); 4.7 for Ti (26.1 nmol/kg), Ba (298.2 nmol/kg) and Cr (1.24 µmol/kg); 4.6 for Al (0.53 mmol/kg).

The relative mobility (the water concentration divided by the rock composition, of major, minor and trace elements) increased considerably during the CO_2-pulses compared to the mobility before and after the CO_2-pulses (Figs. 3a, b and c). The mobility of individual elements was time dependent, reflecting the pH dependence of the maximum concentrations of the elements in the CO_2-charged water as described in the previous paragraph. The elements with the highest (B, Mo, K,) and the lowest (Al, Fe, Ti) mobility during the water conditioning of the column (Fig. 3b) are also among the most and the least mobile elements in natural basaltic groundwater and surface water systems [21, 22]. During the CO_2-pulses the relative mobility for all but one element (V) increased, as shown in Fig. 3a. The most mobile elements were Sr, Mn, K, Cd, Mo, B, and Ti is still among the least mobile elements. Many dissolved elements with the concentrations below the detection limits during the conditioning of the column (Cd, As and REE) increased considerably in concentrations during the CO_2-pulses. The enrichment ratio (the relative mobility during the CO_2-pulses, divided by the relative mobility during the DI water conditioning of the column) is shown in Fig. 3c. The relative mobility increased more than 100 times for Sr, Fe, Al, Ca, Ba, Mn, and Mg. Of these elements, all but Al, can bind with carbonate to form carbonate minerals.
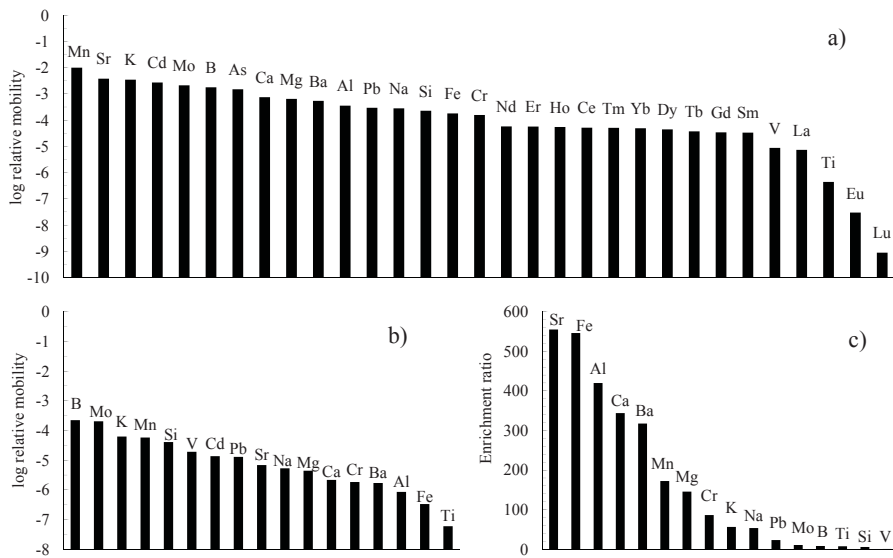
Fig. 3. The relative mobility of the measured elements in sampled solution: a) the maximum relative mobility during the CO_2-pulses, b) the steady-state relative mobility during the conditioning of the column, c) the enrichment ratio of the measured elements during both CO_2-pulses.

According to the European Directive relating to the quality of the water intended for human consumption (80/778/EEC) [23], only the dissolved Al, Fe, Cr and Mn, exceeded allowable drinking water limits (Fig. 4). All of the other measured elemental concentrations were below the drinking water limits. Dissolved Al^{+3} is toxic to plants and animals [24]. High concentration of manganese affects the human nervous system, respiratory tract and the brain. Similarly, iron can accumulate in vital organs, such as the pancreas, liver and heart. Stored iron produces free radicals, which can cause tissue damage, inflammation and organ failure. High concentration of chromium in the surface waters can damage the gills of fish. In animals chromium can cause respiratory problems, a lower ability to fight diseases, birth defects, infertility and tumor formation. The health hazards associated with exposure to chromium are dependent on its oxidation state. The hexavalent form is toxic and carcinogenic [25].

According to the PHREEQC modeling of the outlet solution, the most abundant dissolved Al species was the toxic Al^{+3}. This is due to the low pH, during the CO_2-pulses. During the recovery of the system to its pH neutrality, the dissolved Al species changed to less toxic Al-OH species and the overall concentration decreased (Fig. 4). Speciation of the dissolved Cr did not change during the experimental stages and it was mostly in the Cr^{+3} form, which is not dangerous for human health. Mixing of the CO_2-pulse water with oxygen rich water can make the dissolved Cr carcinogenic by oxidizing it to Cr^{+6}. On the other hand mixing with oxygen rich water will oxidize Fe^{+2} to Fe^{+3}, which will cause the less soluble Fe^{+3} to precipitate as Fe-oxy-hydroxides and lower Fe concentration in the solution. The Fe-oxy-hydroxides could furthermore scavenge toxic metals like the Cr^{+6}.

The pH can govern the mobility of the toxic metals through its effect on the surface charge. At low pH metals show zero sorption to surfaces [26]. The surfaces are positively charged meaning that the cations

will not be adsorbed, despite the fact that secondary Al-, Fe-, Si- phases can potentially precipitate and create a surface to adsorb the metals on. When the pH increases, due to dilution/dissolution of basalt along the flow path – surfaces become negatively charged resulting in adsorption of metals. The concentrations of the toxic metals Pb, Cd, As and Hg were low during the CO_2-pulses, 1.85, 3.5, 2.5 and 0.05 nmol/kg respectively and were below the drinking water limit. After the CO_2-pulses ended, all the elemental concentrations decreased close-to or even below the concentrations measured during the conditioning of the column. The pH never reached ~9 which was the initial *in situ* pH during the conditioning of the system.
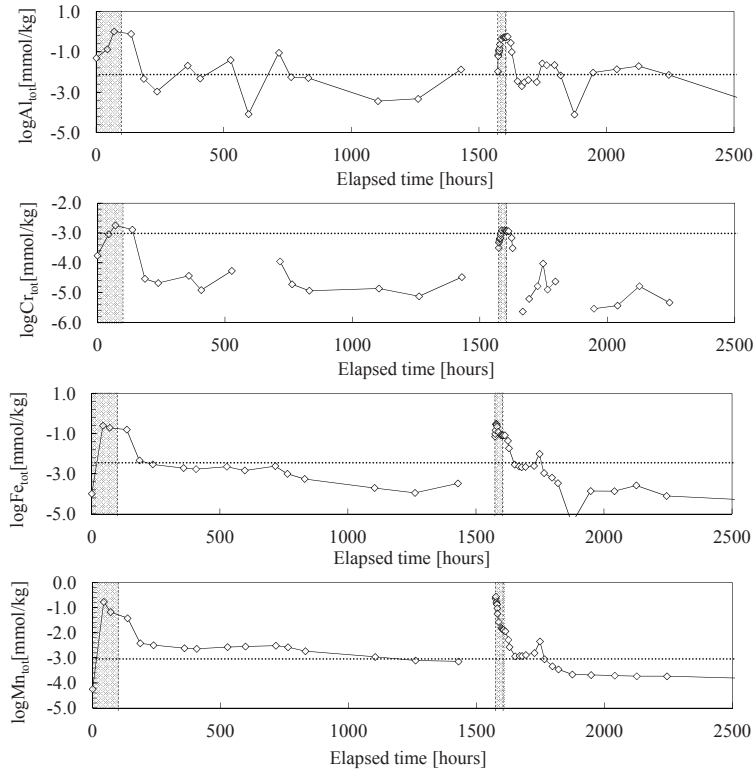

Fig. 4. Total concentrations of the measured elements which exceeded the drinking water limits during the experiment according to the European Directive (80/778/EEC). First data points in all the plots represent the elemental concentrations during the DI water conditioning of the column. Data points in the grey fields correspond to the first and the second CO_2-pulse respectively. All other data points represent the third and the fifth stage when DI water was replacing the CO_2-charged water injected during the CO_2-pulses. Horizontal line is the upper limit for drinking water established by European Commission.

The saturation states of the most important secondary minerals, with respect to the solution during and after the CO_2-pulses, are shown in Fig. 5. The sampled solution was supersaturated with respect to the carbonates: siderite, ankerite and $(Ca,Mg,Fe)CO_3$ just during the first hours of the second CO_2-pulse when the CO_2 was already in the system but the pH was still high enough (~6) to make the water supersaturated with respect to these phases. The solution was supersaturated with respect to gibbsite

during all the experimental stages. The water was most often supersaturated with respect to Si-, Al-, Fe-phases such as amorphous $Al(OH)_3$, goethite, kaolinite and imogolite; however when the pH reached its minimum at ~4.5 the solutions became undersaturated with respect to these phases and supersaturated again after the pH increased to ~6.0. When the second CO_2-pulse started and pH decreased, these secondary Si-, Al-, Fe- phases may have dissolved releasing Si, Al, Fe and also other minor elements which were perhaps scavenged by these secondary phases. According to [27] mineral phases scavenging Cr, Fe and Mn observed in low to neutral pH environments are among others: goethite, amorphous $Fe(OH)_3$ and hematite. In these environments, most of the Al is consumed by amorphous $Al(OH)_3$ and gibbsite limiting Al concentration in solution.
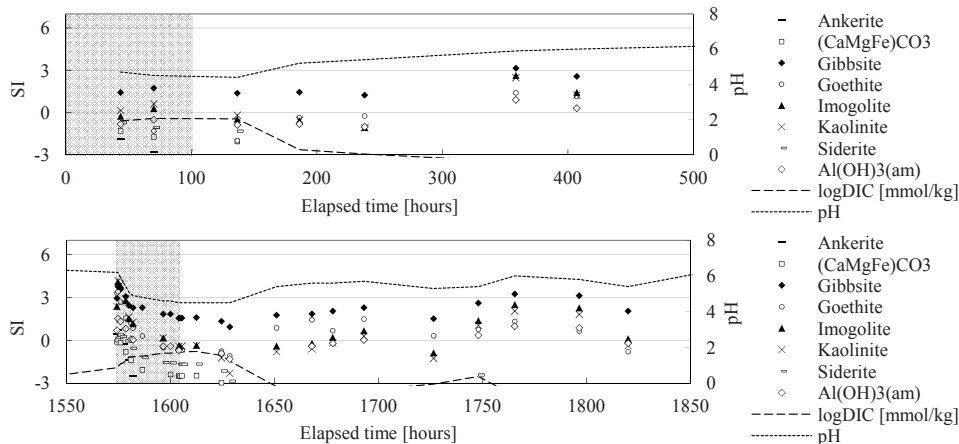

Fig. 5. The saturation indices (SI) of the chosen minerals with respect to the water samples taken during the CO_2-pulses (data points in the shadowed field) and during the recovery of the system when DI water was replacing the CO_2-charged water injected previously. The concentration of DIC was calculated using PHREEQC.

4. Conclusions

The injection of the CO_2-charged water into the high pressure column flow reactor filled with the basalt slurry increased the elemental mobility of basaltic glass constituents significantly. The dissolution rate of basaltic glass is pH dependant. The CO_2-charged water changed the pH conditions from basic/neutral to acidic causing faster dissolution of the rock. The laboratory experimental CO_2-pulses described in this study mimicked very well natural processes such as magmatic CO_2 admixture into the groundwater systems [28] or industrial CO_2 storage when the CO_2-charged water is injected into basaltic aquifers [5, 6]. Basalt releases not only elements essential for life but also those that are toxic and dangerous for the environment. Results of the experiment showed high concentrations of potentially harmful elements such as Cr and Al. Other elements such as Fe and Mn can be dangerous if the concentration exceeds the drinkable limit and this happened during the experimental CO_2-pulses. Elements released from the host rock can pose an environmental problem and their mobility and fate have to be considered and monitored when designing the CO_2 injection system for CO_2 storage.

Saturation state calculations indicate that carbonate precipitation could happen just in the beginning of the CO_2-pulse when the water was still at neutral pH but the release rate of divalent elements such as Fe, Ca, and Mg was high enough to reach saturation with respect to the carbonate minerals. Similar conditions

may occur during the industrial injection of CO_2 at some distance from the injection well when dilution and/or H_2O-CO_2-basalt interaction will increase the pH in presence of CO_2. Other phases which could precipitate from the experimental solution were Fe-, Al-, Si- phases which immobilize the toxic Al and in addition can scavenge other toxic elements such as Cr. The pH and Eh conditions will play a crucial role in elemental speciation and have to be considered during the CO_2 injection.

Acknowledgements

References

[1] E.H. Oelkers, S.R. Gislason, J. Matter, *Mineral Carbonation of CO_2*, Elements, 4 (2008) 333-337.
[2] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (Eds.), *IPCC Special Report on Carbon Dioxide Capture and Storage*. Cambridge University Press, New York (2005).
[3] B.P. McGrail, H.T. Schaef, A.M. Ho, Y.-J. Chien, J.J. Dooley, C.L. Davidson, *Potential for carbon dioxide sequestration in flood basalts*, J. Geophys. Res., 111 (2006) B12201.
[4] C. Dessert, B. Dupré, J. Gaillardet, L.M. François, C.J. Allègre, *Basalt weathering laws and the impact of basalt weathering on the global carbon cycle*, Chemical Geology, 202 (2003) 257-273.
[5] S.R. Gislason, D. Wolff-Boenisch, A. Stefansson, E.H. Oelkers, E. Gunnlaugsson, H. Sigurdardottir, B. Sigfusson, W.S. Broecker, J.M. Matter, M. Stute, G. Axelsson, T. Fridriksson, *Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project*, International Journal of Greenhouse Gas Control, 4 (2010) 537-545.
[6] E.S.P. Aradóttir, E.L. Sonnenthal, G. Björnsson, H. Jónsson, *Multidimensional reactive transport modeling of CO_2 mineral sequestration in basalts at the Hellisheidi geothermal field, Iceland*, International Journal of Greenhouse Gas Control, 9 (2012) 24-40.
[7] B.P. McGrail, F.A. Spane, E.C. Sullivan, D.H. Bacon, G. Hund, *The Wallula basalt sequestration pilot project*, Energy Procedia, 4 (2011) 5653-5660.
[8] H.T. Schaef, B.P. McGrail, A.T. Owen, *Carbonate mineralization of volcanic province basalts*, International Journal of Greenhouse Gas Control, 4 (2010) 249-261.
[9] A.P. Gysi, A. Stefánsson, *Mineralogical aspects of CO_2 sequestration during hydrothermal basalt alteration — An experimental study at 75 to 250°C and elevated pCO_2*, Chemical Geology, 306–307 (2012) 146-159.
[10] H.T. Schaef, B.P. McGrail, A.T. Owen, *Basalt Reactivity Variability with Reservoir Depth in Supercritical CO_2 and Aqueous Phases*, Energy Procedia, 4 (2011) 4977-4984.
[11] T.K. Flaathen, S.R. Gislason, E.H. Oelkers, Á.E. Sveinbjörnsdóttir, *Chemical evolution of the Mt. Hekla, Iceland, groundwaters: A natural analogue for CO_2 sequestration in basaltic rocks*, Applied Geochemistry, 24 (2009) 463-474.
[12] I. Galeczka, D. Wolff-Boenisch, T.H. Jonsson, B. Sigfusson, A. Stefansson, S.R. Gislason, *A novel high pressure column flow reactor for experimental studies of CO_2 mineral storage*, Applied Geochemistry.
[13] E.H. Oelkers, S.R. Gislason, *The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25°C and pH = 3 and 11*, Geochimica et Cosmochimica Acta, 65 (2001) 3671-3681.
[14] D. Wolff-Boenisch, S. Wenau, S.R. Gislason, E.H. Oelkers, *Dissolution of basalts and peridotite in seawater, in the presence of ligands, and CO2: Implications for mineral sequestration of carbon dioxide*, Geochimica et Cosmochimica Acta, 75 (2011) 5510-5525.
[15] G.J. Stockmann, D. Wolff-Boenisch, S.R. Gislason, E.H. Oelkers, *Do carbonate precipitates affect dissolution kinetics? 1: Basaltic glass*, Chemical Geology, 284 (2011) 306-316.
[16] D.L. Parkhurst, C.A.J. Appelo, *User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.* USGS-Report 99-4259.
[17] A.P. Gysi, A. Stefánsson, *CO_2–water–basalt interaction. Numerical simulation of low temperature CO_2 sequestration into basalts*, Geochimica et Cosmochimica Acta, 75 (2011) 4728-4751.

[18] A. Stefánsson, S.R. Gíslason, *Chemical Weathering of Basalts, Southwest Iceland: Effect of Rock Crystallinity and Secondary Minerals on Chemical Fluxes to the Ocean*, American Journal of Science, 301 (2001) 513-556.

[19] K.L. Rogers, P.S. Neuhoff, A.K. Pedersen, D.K. Bird, *CO_2 metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland*, Lithos, 92 (2006) 55-82.

[20] S.R. Gislason, H.P. Eugster, *Meteoric water-basalt interactions. II: A field study in N.E. Iceland*, Geochimica et Cosmochimica Acta, 51 (1987) 2841-2855.

[21] E.S. Eiriksdottir, P. Louvat, S.R. Gislason, N. Óskarsson, J. Hardardóttir, *Temporal variation of chemical and mechanical weathering in NE Iceland: Evaluation of a steady-state model of erosion*, Earth and Planetary Science Letters, 272 (2008) 78-88.

[22] S.R. Gíslason, Á. Snorrason, H.K. Kristmannsdóttir, Á.E. Sveinbjörnsdóttir, P. Torsander, J. Ólafsson, S. Castet, B. Dupré, *Effects of volcanic eruptions on the CO_2 content of the atmosphere and the oceans: the 1996 eruption and flood within the Vatnajökull Glacier*, Iceland, Chemical Geology, 190 (2002) 181-205.

[23] European Community. *Council directive 80/778/EC of 15 July 1980 relating to the quality of water intended for human consumption as amended by Council Directives 81/858/EEC and 91/692/EEC (further amended by Council Regulation 1882/2003/EC.*

[24] R.W. Gensemer, R.C. Playle, *The Bioavailability and Toxicity of Aluminum in Aquatic Environments*, Critical Reviews in Environmental Science and Technology, 29 (1999) 315-450.

[25] N.K. Chandra Babu, K. Asma, A. Raghupathi, R. Venba, R. Ramesh, S. Sadulla, *Screening of leather auxiliaries for their role in toxic hexavalent chromium formation in leather—posing potential health hazards to the users*, Journal of Cleaner Production, 13 (2005) 1189-1195.

[26] C.A.J. Appelo, D. Postma, *Geochemistry, groundwater and pollution*. 2nd ed. Amsterdam: CRC Press; 2005.

[27] H. Kaasalainen, A. Stefánsson, *The chemistry of trace elements in surface geothermal waters and steam*, Iceland, Chemical Geology, 330–331 (2012) 60-85.

[28] I. Galeczka, D. Wolff-Boenisch, S.R. Gislason. *Experimental studies on CO_2 sequestration in basaltic rocks with a plug flow reactor*. Goldschmmidt 2011 Conference Abstracts, Mineralogical Magazine, 75(3) (2011) 883.