
HyUSPRe

Hydrogen Underground Storage in Porous Reservoirs

Assessment of the impact of CH₄ and CO₂ on the geochemical response of the hydrogen- brine-rock system

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Executive summary

This report describes a series of experiments designed to investigate the possible geochemical impacts of utilising natural gas, consisting of 70-90% methane (CH₄) or CO₂ as a cushion gas during H₂ storage operations. This work was carried out to address a current gap in experimental data for ground-truthing predictions of the behaviour of such systems.

Experiments were carried out using samples of two reservoir rocks and one caprock. Each rock type was crushed, immersed in a 3.5% NaCl brine, and subjected to gas pressures (c. 60 bar) of various compositions for periods of up to 68 days within stainless steel pressure vessels housed in an oven set to 80°C. Gases used were H₂, CO₂, CH₄, N₂ and a 50:50 H₂:CO₂ and H₂:CH₄ mixture. Control runs were also carried out using no solid sample.

At the end of experimental runs a single sample of the reacted brine was collected for elemental analysis via ICP-OES. This allowed direct comparison of net elemental release between runs, allowing estimation of the relative contributions to reaction of H₂, CH₄ and CO₂.

The results with CO₂ indicate that, where reaction is dependent on the gas phase, reactions related to the presence of CO₂ are dominant. Significant carbonate and some silicate dissolution was identified during runs using CO₂, with similar responses whether it was pure CO₂ or 50:50 CO₂ and hydrogen, while runs using H₂ only showed little gas dependant reaction. Reaction independent of the gas phase also occurred, including likely ion exchange reaction between the reacting brine and micas present in the solid and minor sulphate dissolution.

The results with methane show that the addition of CH₄ to the systems had no observable effect in terms of the fluid chemistry.

These results may be taken as favourable for hydrogen storage with a carbon dioxide or methane cushion gas as they indicate little short-term reaction involving hydrogen itself (i.e. the hydrogen stored should remain largely unchanged). There were notable reactions involving CO₂, which may lead to increased CO₂ storage security through solubility and mineral trapping. The CO₂ rock reactions may also influence the porosity and permeability of the reservoir.

This work was carried out under abiotic conditions, and it is noted that microbially mediated reactions involving hydrogen, especially in combination with CO₂, may have a larger impact on reservoir geochemistry than was observed here and this may be an important avenue of future investigation.

About HyUSPRe

Hydrogen **U**nderground **S**torage in **P**orous **R**eservoirs

The HyUSPRe project researches the feasibility and potential of implementing large-scale underground geological storage for renewable hydrogen in Europe. This includes the identification of suitable porous reservoirs for hydrogen storage, and technical and economic assessments of the feasibility of implementing large-scale storage in these reservoirs to support the European energy transition to net zero emissions by 2050. The project will address specific technical issues and risks regarding storage in porous reservoirs and conduct an economic analysis to facilitate the decision-making process regarding the development of a portfolio of potential field pilots. A techno-economic assessment, accompanied by environmental, social, and regulatory perspectives on implementation will allow for the development of a roadmap for widespread hydrogen storage by 2050, indicating the role of large-scale hydrogen storage in achieving a zero-emissions energy system in the EU by 2050.

This project has two specific objectives. Objective 1 concerns the assessment of the technical feasibility, associated risks, and the potential of large-scale underground hydrogen storage in porous reservoirs for Europe. HyUSPRe will establish the important geochemical, microbiological, flow, and transport processes in porous reservoirs in the presence of hydrogen via a combination of laboratory-scale experiments and integrated modelling; and establish more accurate cost estimates to identify the potential business case for hydrogen storage in porous reservoirs. Suitable storage sites will be identified, and their hydrogen storage potential will be assessed. Objective 2 concerns the development of a roadmap for the deployment of geological hydrogen storage up to 2050. The proximity of storage sites to large renewable energy infrastructure and the amount of renewable energy that can be buffered versus time varying demands will be evaluated. This will form a basis for developing future scenario roadmaps and preparing for demonstrations.

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1 Introduction

The transition to zero-carbon energy generation from renewable sources requires storing renewable energy intermittently in energy carrier molecules, such as hydrogen (H_2), to overcome imbalances between renewable energy supply and energy demand. Large-scale subsurface storage of H_2 in porous media, e.g. in globally abundant depleted gas fields and saline aquifers, is being considered as an alternative to expensive purpose-built storage containers aboveground.

During hydrogen storage in aquifer (as opposed to volumetric) reservoirs, there is an operational requirement for a cushion gas (or base gas) for retaining the reservoir pressure above a certain minimum pressure as the hydrogen working gas is being withdrawn to meet the contracted minimum deliverability (rate of withdrawal) of the store. Where the difference between the reservoir pressure and wellhead pressure (drawdown), drives production. When using depleted gas reservoirs, natural gas, consisting of 70-90% methane, will act as a cushion gas and there has been work ongoing to explore the potential to use CO_2 as a cushion gas.

Geochemical interactions between the hydrogen gas that has been stored, cushion gas, reservoir fluids, and reservoir minerals may take place. These reactions have the potential to alter the porosity and permeability of the storage reservoir as a result of mineral dissolution or precipitation, impacting the integrity of the reservoir and purity of the produced gasses.

While much work has been done on the likely reservoir impacts of CO_2 injection, thanks to increasing interest in and implementation of geological storage of carbon dioxide, there are fewer studies on the impact of hydrogen and fewer still on the kinds of mixed gas systems which will likely be utilised for hydrogen storage. Experimental data is particularly lacking, and the work herein has been designed to begin to address this data gap.

The following section provides some more background to the study along with identification of what previous work there has been in the area. Thereafter the methodology and results of the current study are presented followed by a discussion of their implications in the context of hydrogen storage and possible further experimental work.

2 Background

During geological storage of hydrogen, the use of a cushion gas will likely be required in order to maintain storage reservoir pressures and to minimise contact between the working gas (hydrogen) and the reservoir brine. The cushion gas would generally be injected ahead of the working gas in order to prepare the reservoir by driving out formation fluid. Working gas is then introduced and removed as necessary, while the cushion gas largely remains in the reservoir. Cushion gas selection may be made on the basis of cost, reservoir conditions, or gas properties (such as density or wettability) (Muhammed et al. 2022) but, in the case of hydrogen will likely be either natural gas (Feldmann et al. 2016), carbon dioxide (Oldenburg 2003), nitrogen (Pfeiffer, Beyer, and Bauer, 2017), or hydrogen itself. Carbon dioxide and natural gas are suggested as they are denser than hydrogen and natural gas may already be present in, e.g., depleted gas reservoirs, while the use of CO₂ has the added benefit of long-term CO₂ storage.

It is also worth noting that these gases may also be present as part of the working gas itself or may be mixed with hydrogen for reasons other than acting as a cushion gas. While hydrogen may be introduced as a pure, or near pure, gas it could also be introduced as part of a mixture of blended hydrogen and natural gas, or as a component of town or syngas (a mixture of CO, CO₂, H₂ and CH₄ produced via gasification of biomass, coal, or other hydrocarbon feedstock), or may be introduced to an existing store of CO₂ in order to promote methanation of hydrogen and carbon dioxide via bacterial methanogenesis (Panfilov 2016).

While the feasibility of large scale underground hydrogen storage (UHS) has been studied for several decades there are few sites where it has been put into practice and experience in UHS is limited, especially in terms of working with a mix of gases (Zivar, Kumar, and Foroozesh 2021) and hence much current work in the area is reliant on modelling or experimental studies.

In terms of the interplay between hydrogen, other gases present and the reservoir system a number of recent studies have been produced focussing on modelling the physical aspects of these systems in terms of gas injection and production (Heinemann et al. 2021; Feldmann et al. 2016; Zamehrian and Sedaei 2022), thermodynamic and transport properties (Hassanpouryouzband et al. 2020; Zhao, Wang, and Chen 2023), or properties such as contact angle and wettability (Muhammed, Haq, and Al Shehri 2023). Relatively little attention has been given to the possible geochemical processes within the kind of mixed gas systems which may be utilised during hydrogen storage, however.

Much attention has been given to the reaction of CO₂ with formation brines and minerals over the past thirty years thanks to increasing interest in and utilisation of geological carbon storage (GCS) with numerous studies investigating geochemical processes via experimental (Allan, Turner, and Yardley 2011; Bateman et al. 2011; Kaszuba, Yardley, and Andreani 2013; Rosenqvist, Kilpatrick, and Yardley 2012), and modelling (Celia and Nordbotten 2009; Gaus et al. 2008; Portier and Rochelle 2005) work, as well as collection and interpretation of data from natural analogues or operational GCS schemes.

Since large scale underground storage of hydrogen has only recently been given serious consideration, studies on the potential geochemical impacts of hydrogen on reservoir systems are fewer, but recent outputs investigating geochemical issues have included experimental and modelling (Bo et al. 2021; Hassannayebi et al. 2019; Zeng et al. 2022; Saeed, Jadhawar, and Bagala 2023) work. Older studies on hydrogen reactions during long-term storage of radioactive waste also contain data relevant to hydrogen storage (Truche et al. 2013).

Studies of systems where hydrogen is present with other gases are rarer. Some work does exist exploring and identifying possible geochemical impacts of hydrogen storage in depleted gas fields where methane will be present as the main constituent of natural gas (Hemme and van Berk 2018; Shi, Jessen, and Tsotsis 2020; Amid, Mignard, and Wilkinson 2016) and on hydrogen storage with carbon dioxide (Saeed, Jadhawar, and Bagala 2023; Iloejesi and Beekingham 2021). Some relevant data are also available from sites where, for example, town gas has been actively stored (Šmigáň et al. 1990), but overall experimental data to ground truth modelling studies for hydrogen bearing systems in general, but particularly to mixed gas systems is scarce and we hope to begin to address this data gap with the experiments described in this work.

Of the gases discussed in relation to hydrogen storage (H_2 , CO_2 , CH_4 , N_2), it may be reasonably expected that the addition of CO_2 would have the largest geochemical impact for many reservoirs, at least in abiotic systems. The addition of hydrogen and natural gas may have increased impact on reservoir chemistry from microbially-mediated processes, where significant populations of methanotrophs or hydrogenotrophs are present or where their introduction may significantly alter the redox conditions of the system.

Considering CO_2 alone, initial interaction with the reservoir fluid will involve dissolution of CO_2 from the supercritical phase into the reservoir brine, as dictated by local pressure, temperature, and salinity conditions (Rochelle, Czernichowski-Lauriol, and Milodowski 2004). Initially, CO_2 will exist in equilibrium with relatively weak carbonic acid, before it dissociates to bicarbonate or carbonate ions, generating acidity. The acidity or carbonate ions generated during this process may be utilised through fluid-mineral reactions. Initially, acidity may be rapidly neutralised by carbonate dissolution or ion exchange, whereby accessible cations held on mineral surfaces are exchanged for hydrogen ions in solution. The cations released at this stage and through dissolution of primary minerals may include Ca, Mg and Fe ions, which, in turn, can react with carbonate ions in solution leading to secondary carbonate mineral precipitation of, for example, calcite ($CaCO_3$), magnesite ($MgCO_3$), or siderite ($FeCO_3$). Over the longer term slow dissolution of aluminosilicate minerals can also occur (Baines and Worden 2004) and, depending on the mineralogy of the reservoir, could include the reaction of anorthite to calcite and kaolinite; albite to Na-smectite, bicarbonate and quartz; and, in the presence of an NaCl brine, K-feldspar to dawsonite and quartz.

During hydrogen injection, on the other hand, many of the expected reactions are linked to its ability to act as an electron donor (i.e. a reducing agent) in both biotic and abiotic processes (Berta et al. 2018; Thaysen et al. 2021). Such reactions have been proposed to explain changes in gas composition observed at town gas storage sites in Ketzin, Germany, and Beynes, France. At Beynes increased concentrations of hydrogen sulphide were observed and may be explained by the abiotic reduction of pyrite by hydrogen (Reitenbach et al. 2015) although the temperature $25^\circ C$ is more in line with microbial activity. Experience from studies of hydrogen reaction in radioactive waste disposal systems also suggests that abiotic reduction of pyrite to pyrrhotite is also possible (Truche et al. 2010) although this is expected to be slow at temperatures below $120^\circ C$. Other redox related reactions which may occur include reduction of electron acceptors, such as sulphates, carbonates and iron oxides or micas and clays containing ferric iron (Yekta, Pichavant, and Audigane 2018). Dissolution of calcite and anhydrite cements has also been observed experimentally upon exposure to hydrogen (Flesch et al. 2018), possibly due to generation of more acidic conditions as sulphate species are reduced to, e.g., HS^- or H_2S or because the brine used was undersaturated with respect to relevant minerals, although the majority of experimental work available is generally in agreement that very little abiotic reaction occurs between hydrogen and reservoir materials at relevant conditions (Yekta, Pichavant, and Audigane 2018; Hassanpouryouzband et al. 2022). In conditions where significant microbial populations are active then methanogenesis,

acetogenesis and sulphate reduction reactions may occur more readily (Tremosa, Jakobsen, and Le Gallo 2023).

This work aims to explore the reactivity of a small number of reservoir and caprock samples with both hydrogen and carbon dioxide, or hydrogen and methane (as a proxy for natural gas) charged brine in order to better understand the relative impacts of the reactions described above. The methodology behind, and results of, this study are laid out in the following sections.

3 Hydrogen-CO₂ Geochemical experiments

3.1 Methodology

Our sample selection process was aimed to represent specific geological conditions. We prioritised reservoirs where reservoir rocks were readily available, and the composition of the formation fluid was well-documented. Additionally, we sought samples characteristic of the clusters of potential hydrogen storage reservoirs, as defined by Cavanagh et al., 2022, 2023 (HyUSPre deliverable D1.3 and D1.5).

Cluster Definitions:

Cavanagh et al. (2022, 2023) classified potential hydrogen storage reservoirs into four distinct clusters based on key geological parameters:

- Northwestern Europe Cluster: These reservoirs are characterized by their significant depth (up to 3300 meters), elevated temperatures (70-115 °C), and high initial gas pressure (up to 28 MPa).
- Central Europe Cluster: Reservoirs in this cluster are situated at intermediate depths (400-1550 meters) with temperatures below 60 °C and initial gas pressure lower than 20 MPa.
- Eastern Europe Cluster: Similar to the Central Europe Cluster, these reservoirs are characterized by intermediate depths (400-1550 meters) and lower temperatures below 60 °C.
- Southern Europe Cluster: Reservoirs in this cluster also exhibit intermediate depths (400-1550 meters) and lower temperatures below 60 °C.

Selected Samples:

From the available materials, we identified two reservoirs that met our specified criteria:

- Field 1: Eastern Europe Cluster - Reservoir rocks and caprocks from an anonymized gas field were provided by HGS. These samples closely resemble these reservoirs are characterized by intermediate depths (400-1550 meters) and lower temperatures below 60 °C.
- Field 2: Northwestern Europe Cluster – Reservoir rocks and caprocks from an anonymized gas field were provided by Centrica. These samples closely resemble the deepest reservoirs, with depths of 3300 meters and formation temperatures of these reservoirs are characterized by their significant depth (up to 3300 meters), elevated temperatures (70-115 °C), and high initial gas pressure (up to 28 MPa).

Three rock samples, supplied by project partners, were used in a series of experiments designed to investigate the geochemical impact of CO₂ on brine-rock-hydrogen systems.

These samples comprised AGH0005, a sandstone reservoir sample from the Upper Pannonian sediments of the Field 1, Hungary, AGH0006, a siltstone caprock sample from the same field, and AGH0007, a sandstone reservoir sample from Field 2, United Kingdom. For use in the experiments, samples were crushed and sieved to a <350 µm fraction. Gross sample mineralogy was determined by X-ray diffraction (Bruker D8 - Powder Diffractometer: scanning parameters 0–90°, 2θ, accuracy in peak positions ≤0.01 2θ, Bragg–Brentano configuration). Mineral phases were identified using the internal Bruker database with EVA analysis package, and weight percentages (wt %) were quantified by Rietveld analysis. This analysis is summarised in Table 1.

Table 1: Summary and XRD analysis of rock samples used in this work.

Lab Sample ID	Partner ID	Partner	% Quartz	% K feldspar	% Chlorite	% Mica	% Dolomite	% Calcite	% Plagioclase	Notes/Description
AGH0005	A12#12	HGS	51.1	11.7	11.9	8.3	9	2.9	4.6	Field 1, 1234 m depth (reservoir rock)
AGH0006	A12#11	HGS	43.1	2	12.9	18.1	9.9	3.1	10.4	Field 1, 1225 m depth (caprock)
AGH0007	R1	Centrica	89.5	1.8	1.3	1.5	2.8	ND	3.2	Field 2, 3023 m depth (reservoir rock)

These crushed samples were used, together with a solution of 3.5% NaCl (supplied by Fisher Scientific, 99.5% purity), in batch reaction experiments using either hydrogen, carbon dioxide, nitrogen (all supplied by BOC, research grade, 99.9995% purity), or a 50%-50% mixture of hydrogen and carbon dioxide as the pressurising medium.

Experiments were carried out in custom designed 316 stainless steel reaction vessels, made at the University of Edinburgh. For experimental runs, each vessel was stacked with a series of glass containers each holding 15 g of crushed rock sample (except for brine only control runs) and 50 g 3.5% NaCl solution. Vessels were then sealed and placed in a fan oven (SciQuip Oven-110S). Following evacuation (to remove free oxygen), using a CPS VP2S pro-set single-stage vacuum pump, vessels were pressurised with either H₂, CO₂, N₂, or the H₂-CO₂ mixture. During runs vessel pressure and temperature conditions were measured continuously using a GD4200-US Digital Pressure Transducer from Elemental Science Inc. Data were recorded on a PC at 1 min intervals; the measurement errors for pressure and temperature were quantified as $\pm 0.15\%$ span best fit straight line and $\pm 1.5\%$ FS total band, respectively.

Experimental runs were carried out at 80°C and at a target/starting pressure of 60 bar. Note that due to leakage over time the average pressure during some runs fell below this target (see Table 2). All runs lasted for a duration of 68 days, at the end of which vessels were depressurised and a liquid sample retrieved from each of the glass containers and filtered through a 0.2 µm nylon filter, with a split taken and acidified for ICP-OES analysis. Measurements of pH and conductivity were made on these samples followed by compositional analysis via inductively coupled plasma–optical emission spectroscopy (ICP-OES) using a Varian Vista Pro with APEX-E from Elemental Science Inc. (LoD of 0.105 × 10³ to 0.26 ppm or ~ 0.2–100 ppb).

A schematic of the experimental set-up is shown in Figure 1, while a summary of the experiments carried out is presented in Table 2.

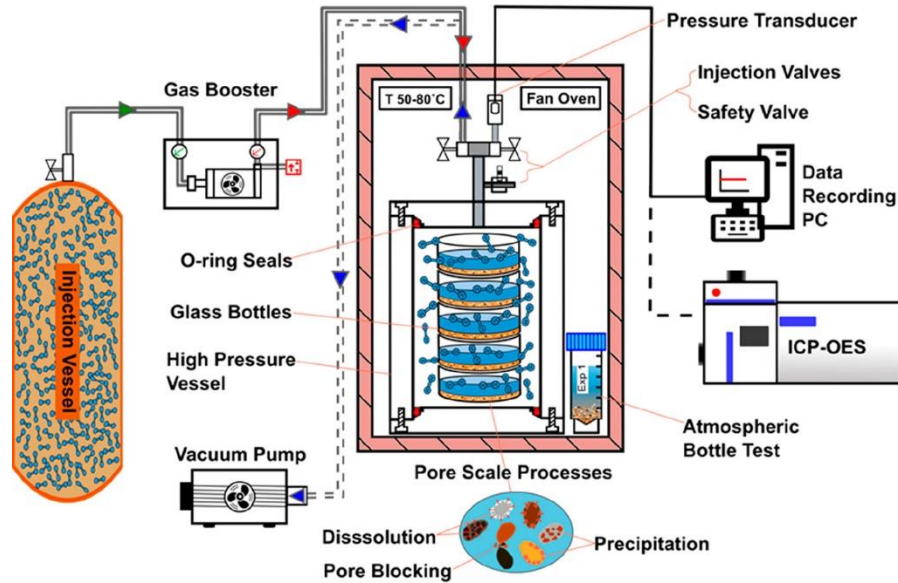


Figure 1: Schematic of experimental set-up.

Table 2: Experimental Run Summary.

Run ID	Solid	Solid Weight (g)	Temperature (°C)	Average Pressure (bar)	Gas	Starting fluid	Fluid weight (g)	Run Time (days)
1017	AGH0005	15	80	62.8	CO ₂	3.5% NaCl	50	68
1018	AGH0006	15	80	62.8	CO ₂	3.5% NaCl	50	68
1019	AGH0007	15	80	62.8	CO ₂	3.5% NaCl	50	68
1020	Brine only	-	80	62.8	CO ₂	3.5% NaCl	50	68
1021	AGH0005	15	80	56.5	CO ₂ +H ₂	3.5% NaCl	50	68
1022	AGH0006	15	80	56.5	CO ₂ +H ₂	3.5% NaCl	50	68
1023	AGH0007	15	80	56.5	CO ₂ +H ₂	3.5% NaCl	50	68
1024	Brine only	-	80	56.5	CO ₂ +H ₂	3.5% NaCl	50	68
1025	AGH0005	15	80	53.4	H ₂	3.5% NaCl	50	68
1026	AGH0006	15	80	53.4	H ₂	3.5% NaCl	50	68
1027	AGH0007	15	80	53.4	H ₂	3.5% NaCl	50	68
1028	Brine only	-	80	53.4	H ₂	3.5% NaCl	50	68
1029	AGH0005	15	80	49.3	N ₂	3.5% NaCl	50	68
1030	AGH0006	15	80	49.3	N ₂	3.5% NaCl	50	68
1031	AGH0007	15	80	49.3	N ₂	3.5% NaCl	50	68
1032	Brine only	-	80	49.3	N ₂	3.5% NaCl	50	68

3.2 Results

For each solid sample four experimental runs were carried out, comprising runs using CO₂ only, H₂ only, a c. 50%-50% mixture of CO₂ and H₂ and a N₂ control. At the end of the experimental runs, lasting c. 68 days, a single fluid sample was retrieved from each run and analysed for pH, conductivity and elemental concentrations (via ICP-OES). This approach allows for a broad comparison of reactivity (via net elemental release) between runs and, hence, a comparison between systems containing only CO₂ or H₂ and those containing gas mixtures.

In addition, control runs were carried out with no solid samples. Other than the omission of the solids, these runs were carried out in exactly the same manner as described above. Select, post-reaction, element concentrations for these control runs are presented in Figure 2, with full analytical results presented in Table 3.

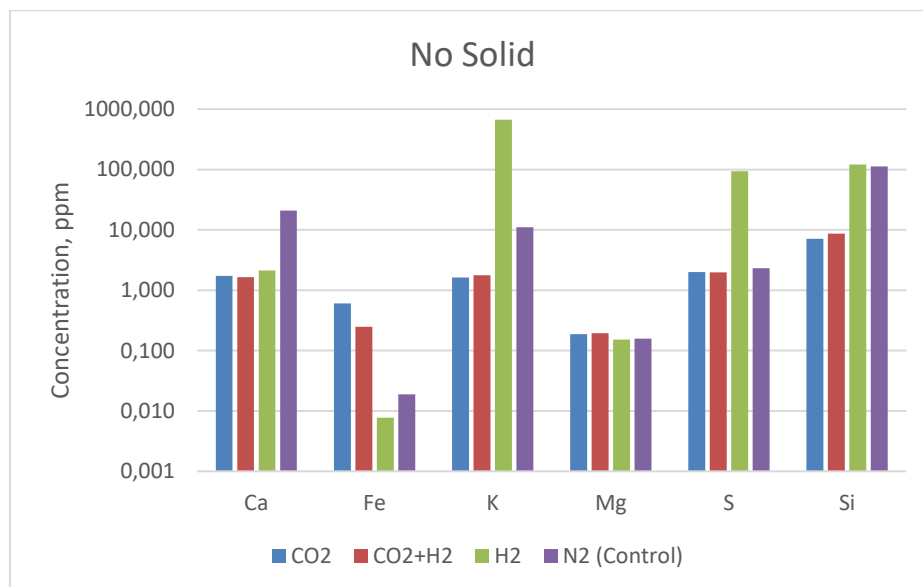


Figure 2: Select elemental concentrations for brine only control runs.

Table 3: Analytical results for fluid samples from brine only control runs.

Run		1020	1024	1028	1032
Gas		CO ₂	CO ₂ +H ₂	H ₂	N ₂
Solid		Brine only	Brine only	Brine only	Brine only
Final pH		7.33	7.32	NM	8.36
Final Conductivity (µs/cm)		59150	58806	NM	60556
Analyte	LoD (ppm)	Concentration, ppm			
Ag	0.0004	BD	BD	BD	BD
Al	0.0101	0.192	0.109	BD	BD
B	0.0153	BD	BD	0.496	BD
Ba	0.0001	0.004	0.003	0.078	0.047
Ca	0.0014	1.736	1.646	2.121	20.822
Cd	0.0003	BD	BD	BD	BD
Ce	0.0005	BD	0.001	BD	BD
Co	0.0002	0.001	BD	0.004	0.001
Cr	0.0016	BD	BD	BD	BD
Cu	0.0009	0.006	BD	BD	BD
Fe	0.0008	0.606	0.249	0.008	0.019
Ga	0.0005	BD	0.001	0.001	BD
Hg	0.0033	0.005	0.011	0.007	0.007
K	0.0011	1.627	1.760	671.500	10.991
Mg	0.0058	0.187	0.194	0.152	0.158
Mn	0.0001	0.001	BD	BD	BD
Na	0.0886	11258	11813	12167	11059
Ni	0.0029	0.003	0.009	BD	0.003
P	0.0018	0.029	0.038	0.775	0.048
Pb	0.0057	BD	BD	BD	BD
S	0.1529	2.003	1.967	94.053	2.319
Si	0.0083	7.158	8.677	120.643	112.836
Sr	0.0000	0.020	0.010	0.011	0.030
Ti	0.0000	BD	BD	BD	BD
Zn	0.0001	0.008	0.006	0.004	0.002
Zr	0.0002	BD	BD	0.000	0.001

Table 4: Analytical results for fluid samples from brine only control runs.

AGH0005

Four experiments were carried out using sample AGH0005. The sample was taken from a well in the Komlós A-1 reservoir from a depth of 1234 m and is of the sandstone reservoir rock. Full analytical results for the runs carried out using this sample are presented in Table 4, while the concentrations of a selection of common mineral forming elements are presented in Figure 3.

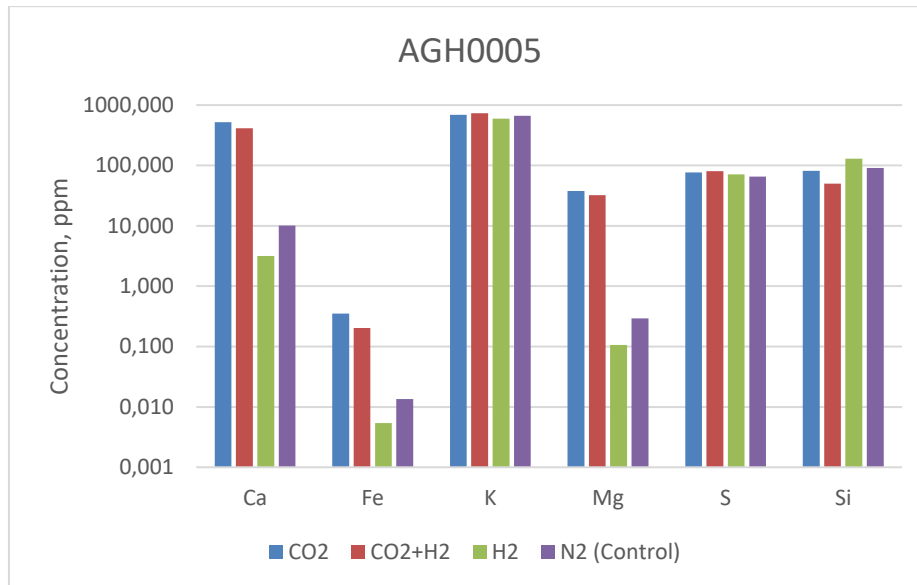


Figure 3: Select elemental concentrations for AGH0005 runs.

Net elemental release is generally higher in the runs using CO₂. This corresponds with the lower pH observed in the CO₂ runs relative to the pH of the CO₂ free runs. pH is lowest (7.3) in the CO₂ only run, corresponding to the highest pCO₂. pH is slightly higher (7.7) in the CO₂/H₂ mixture run and notably higher in the H₂ and N₂ only runs (9.1 and 9.0, respectively).

Ca and Mg are notably elevated in the CO₂ runs relative to the CO₂ free and brine only runs and this is likely indicative of carbonate dissolution: in this case dissolution of calcite (preferentially) and dolomite in the starting material. Carbonates, particularly calcite, are susceptible to dissolution under the acidic conditions induced by elevated pCO₂ and primary carbonates are often found to be relatively reactive under such conditions (e.g., Bateman et al. 2011).

Al concentrations were below detection in all runs while K was notably elevated in all runs. The elevated potassium concentrations are not reflected in the runs carried out with no solid (other than in the H₂ run, which likely reflects a contamination issue). The likeliest sources of potassium in the experiments are k-feldspar and biotite. Wholesale dissolution of these minerals would, however, be reflected in similarly elevated Al concentrations which are not observed. It is possible, therefore, that the elevated K concentrations observed are due to relatively rapid ion exchange reactions, for example between Na in the starting brines and K on biotite surfaces. This process seems to be broadly independent of the gas composition. Some wholesale dissolution of aluminosilicate minerals may also be occurring (see results for Si, below), with Al release being 'masked' by secondary precipitation of, e.g., clay minerals.

Fe concentrations in the runs were similar to those in runs carried out with no solid (see Figure 2) and showed a similar trend of higher concentrations in the CO₂ runs. This may be indicative of contamination through leaching of some component of the experimental system: either

leaching of the steel wall of the vessel by CO₂ and subsequent transfer to the reacting fluid or from impurities in the glass containers used to hold the experiments within the steel vessels.

Table 5: Analytical results for AGH0005 runs.

Run		1017	1021	1025	1029
Gas		CO ₂	CO ₂ +H ₂	H ₂	N ₂
Solid		AGH0005	AGH0005	AGH0005	AGH0005
Final pH		7.29	7.66	9.13	9.00
Final Conductivity (µs/cm)		62568	62978	59530	63655
Analyte	LoD (ppm)	Concentration, ppm			
Ag	0.0004	0.001	0.001	BD	0.000
Al	0.0101	BD	BD	BD	BD
B	0.0153	0.495	0.537	0.472	0.375
Ba	0.0001	0.959	1.175	0.096	0.671
Ca	0.0014	521.351	412.422	3.161	10.146
Cd	0.0003	BD	BD	BD	BD
Ce	0.0005	BD	BD	BD	BD
Co	0.0002	0.028	0.005	0.001	0.002
Cr	0.0016	BD	BD	BD	BD
Cu	0.0009	BD	0.002	BD	BD
Fe	0.0008	0.353	0.202	0.005	0.013
Ga	0.0005	0.003	0.002	BD	0.001
Hg	0.0033	0.005	0.007	BD	BD
K	0.0011	689.999	730.149	592.914	667.881
Mg	0.0058	37.823	32.153	0.106	0.293
Mn	0.0001	0.218	0.112	BD	0.007
Na	0.0886	11340	11676	11050	11808
Ni	0.0029	0.114	0.042	0.010	0.006
P	0.0018	0.037	0.042	0.476	0.271
Pb	0.0057	BD	BD	BD	BD
S	0.1529	76.543	80.052	71.162	65.223
Si	0.0083	81.770	50.121	130.162	91.304
Sr	0.0000	1.801	1.654	0.015	0.876
Ti	0.0000	BD	BD	BD	BD
Zn	0.0001	0.013	0.004	0.002	0.003
Zr	0.0002	0.005	0.004	0.000	BD

There is notable Si release in all runs, including the brine only runs, with the runs without CO₂ showing higher concentrations. This is indicative of dissolution of the glass containers used in the experiments: glass (as well as quartz) has higher solubility at elevated pH. It should be noted that dissolution of the glass containers would also likely lead to contamination by Na, K, Fe, Mg and Ca, amongst other elements (as illustrated by the results of the brine only control runs). The two runs using AGH0005 with CO₂ do have considerably elevated Si concentrations relative to the comparable blank runs without solid, indicating that dissolution of the solid starting material does have a contributing effect in these runs. This likely reflects feldspar dissolution.

Sulphur concentrations are elevated in all runs relative to their solid-free counterparts (with the exception of the hydrogen run, again, likely reflecting a contamination issue). Although not

identified in the XRD analysis, this likely reflects dissolution of gypsum/anhydrite from the starting solid, driven by reaction with the starting brine and, given the narrow range of concentrations (ranging from 65 – 80 ppm) across different runs, largely independent of the gas used. Also pyrite is not detected by XRD, but could be present below the detection limit, and dissolved, possibly through oxidation with remaining oxygen in the system.

AGH0006

Four experiments were carried out using sample AGH0006. AGH0006 is a sample of siltstone caprock supplied by Hungarian Gas Storage and was taken from a well in the Komlós A-1 reservoir from a depth of 1225 m. Full analytical results for these runs are presented in Table 5, while the concentrations of common mineral forming elements are presented in Figure 4. Note that no analysis of the fluid from the N₂ control run was carried out.

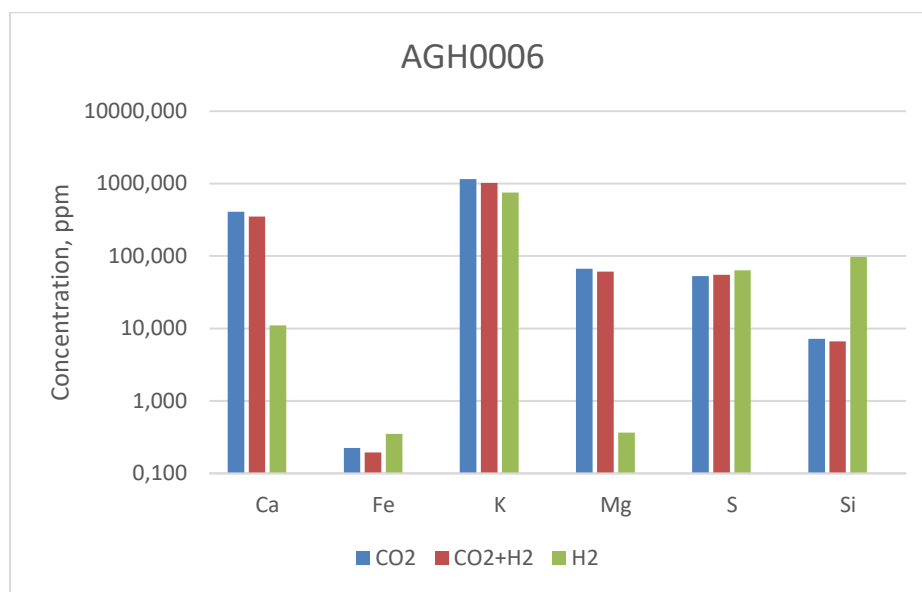


Figure 4: Select elemental concentrations for AGH0006 runs.

As for the experiments carried out using AGH0005 net elemental release shows a strong positive correlation with pCO₂ and, hence, the lower pH observed in CO₂ runs relative to the H₂ or N₂ only runs. pH is lowest (6.8) in the CO₂ only run, corresponding to the highest pCO₂. pH is slightly higher (6.9) in the CO₂/H₂ mixture run and notably higher in the H₂ and N₂ only runs (8.8 in both).

As for the AGH0005 runs Ca and Mg concentrations are considerably higher in the runs where CO₂ was used, indicative of calcite and dolomite dissolution in the presence of dissolved CO₂.

As for the AGH0005 runs Al concentrations were below detection in all runs while K was notably elevated. The elevated potassium concentrations are not reflected in the runs carried out with no solid (other than in the H₂ run, which likely reflects another contamination issue). Relative to AGH0005, AGH0006 has low levels of K-feldspar and a higher amount of mica and so the likeliest source of potassium in these runs is biotite. Again, this may be due to relatively rapid ion exchange reactions, for example between Na in the starting brines and K on biotite surfaces. This process seems to be broadly independent of the gas composition although the K concentrations in the CO₂ runs are elevated relative to H₂ only run, indicating some enhanced leaching in the presence of dissolved CO₂. Some wholesale dissolution of aluminosilicate minerals may also be occurring (see results for silica), with Al release being 'masked' by secondary precipitation of, e.g., clay minerals.

As for AGH0005 Fe concentrations in the runs were similar to those in runs carried out with no solid (see Figure 2) and, again, is indicative of a contamination issue.

Table 6: Analytical results for AGH0006 runs.

Run		1018	1022	1026	1030
Gas		CO ₂	CO ₂ +H ₂	H ₂	N ₂
Solid		AGH0006	AGH0006	AGH0006	AGH0006
Final pH		6.83	6.91	8.77	8.75
Final Conductivity (µs/cm)		60092	64840	61381	60749
Analyte	LoD (ppm)	Concentration, ppm			
Ag	0.0004	0.003	0.002	0.001	Not analysed
Al	0.0101	BD	BD	BD	
B	0.0153	0.484	0.590	0.385	
Ba	0.0001	1.498	1.990	1.315	
Ca	0.0014	410.566	351.756	11.086	
Cd	0.0003	0.001	BD	BD	
Ce	0.0005	BD	BD	0.001	
Co	0.0002	0.023	0.006	0.004	
Cr	0.0016	BD	BD	BD	
Cu	0.0009	BD	0.001	BD	
Fe	0.0008	0.225	0.194	0.350	
Ga	0.0005	0.002	0.003	0.001	
Hg	0.0033	0.011	BD	BD	
K	0.0011	1151.557	1021.208	756.411	
Mg	0.0058	67.116	60.861	0.364	
Mn	0.0001	0.263	0.122	0.004	
Na	0.0886	11601	11847	11822	
Ni	0.0029	0.030	0.021	0.011	
P	0.0018	0.055	0.059	0.227	
Pb	0.0057	BD	BD	BD	
S	0.1529	53.153	55.358	63.584	
Si	0.0083	7.220	6.668	97.824	
Sr	0.0000	3.933	3.954	0.931	
Ti	0.0000	BD	BD	BD	
Zn	0.0001	0.003	0.004	0.005	
Zr	0.0002	0.008	0.008	0.001	

As for AGH0005 there is notable Si release in all runs, including the brine only runs, with the runs with highest pH (without CO₂) showing higher concentrations and, as per AGH0005, this is indicative of dissolution of the glass containers used in the experiments. Unlike AGH0005 the two runs using AGH0006 with CO₂ do not have elevated Si concentrations relative to the comparable blank runs without solid, indicating that dissolution of the solid starting material does not have a contributing effect in these runs. This may be due to the lower amounts of K-feldspar present in this sample, relative to AGH0005.

As for AGH0005 sulphur concentrations are elevated in all runs relative to their solid-free counterparts and, again, likely reflects dissolution minor sulphate present in the samples.

AGH0007

Four experiments were carried out using sample AGH0007. AGH0007 is a sample of sandstone reservoir rock supplied by Centrica and taken from Field 2, from a depth of 3023 m. Full analytical results for these runs are presented in Table 6, while the concentrations of common mineral forming elements are presented in Figure 5.

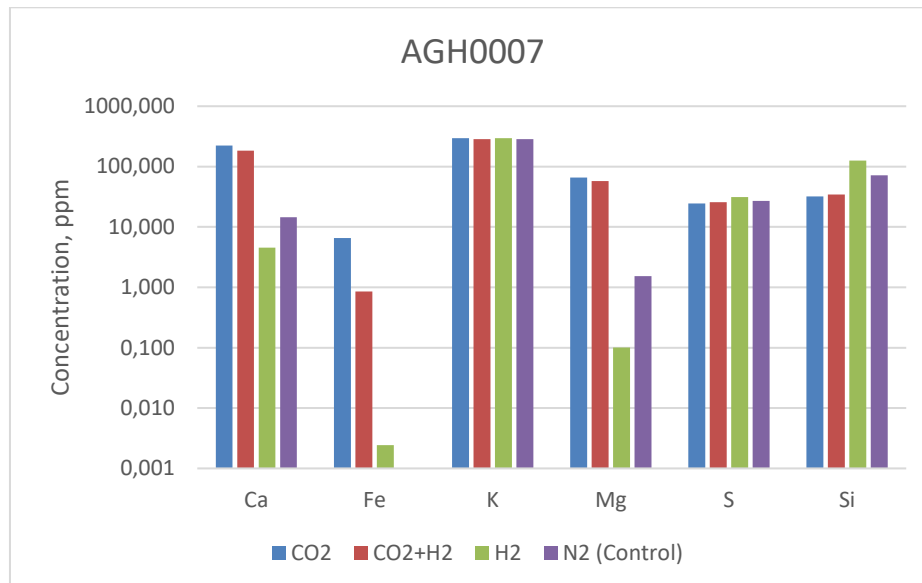


Figure 5: Select elemental concentrations for AGH0007 runs.

Although pH between runs using AGH0007 is much more closely clustered than for other solids used (AGH0005 and AGH0006), there remains a positive correlation between pH and net elemental release, with pH being lower in the CO₂ and CO₂/H₂ runs (7.8 and 7.9 respectively) than in the H₂ and N₂ only runs (8.9 and 8.4, respectively). Net elemental release is notably lower in the runs using this solid than for AGH0005 and AGH0006. This likely reflects the mineralogy which is dominated (90%) by quartz. Feldspars, micas, and carbonate (dolomite only) were detected in the XRD analysis but are present in much lower quantities than for the other solids used in this work (see Table 1).

As for runs using other solids runs Ca and Mg concentrations are considerably higher in the runs where CO₂ was used, indicative of carbonate dissolution in the presence of dissolved CO₂. While runs using other solids showed considerably higher concentrations of Ca compared to Mg, in this case concentrations are closer. This reflects dolomite being the dominant carbonate phase in AGH0007, with little or no calcite present and hence the majority of Ca and Mg are likely sourced via near stoichiometric release exclusively from dolomite.

As for runs using other solids Al concentrations were below detection in all runs while potassium was notably elevated. Again, the likely source of K is the mica present in the sample.

Table 7: Analytical results for AGH0007 runs.

Run		1019	1023	1027	1031
Gas		CO ₂	CO ₂ +H ₂	H ₂	N ₂
Solid		AGH0007	AGH0007	AGH0007	AGH0007
Final pH		7.87	7.76	8.86	8.41
Final Conductivity (µs/cm)		60531	60842	65271	61577
Analyte	LoD (ppm)	Concentration, ppm			
Ag	0.0004	0.001	BD	BD	BD
Al	0.0101	BD	BD	BD	BD
B	0.0153	0.420	0.409	0.377	0.334
Ba	0.0001	1.822	2.043	2.207	2.833
Ca	0.0014	223.772	183.421	4.535	14.464
Cd	0.0003	0.001	BD	BD	BD
Ce	0.0005	BD	BD	0.001	BD
Co	0.0002	0.209	0.094	0.002	0.003
Cr	0.0016	BD	BD	BD	BD
Cu	0.0009	BD	0.006	BD	0.001
Fe	0.0008	6.578	0.853	0.002	BD
Ga	0.0005	0.003	0.002	0.001	0.001
Hg	0.0033	0.008	0.009	0.010	BD
K	0.0011	295.919	284.694	295.081	286.605
Mg	0.0058	65.717	57.489	0.101	1.537
Mn	0.0001	1.377	0.962	BD	BD
Na	0.0886	11090	11138	11727	11727
Ni	0.0029	0.019	0.015	BD	BD
P	0.0018	0.035	0.014	0.028	0.031
Pb	0.0057	BD	BD	BD	BD
S	0.1529	24.466	25.700	31.152	26.906
Si	0.0083	31.990	34.306	125.723	71.381
Sr	0.0000	0.689	0.690	0.091	0.483
Ti	0.0000	BD	BD	BD	BD
Zn	0.0001	0.016	0.006	0.003	0.004
Zr	0.0002	0.002	0.003	BD	0.001

Fe was notably elevated in the CO₂ only run, relative to other AGH0007 runs and to the solid free runs. This is unusual given the relatively low abundance of mica and other accessory minerals in the starting solid and may reflect a contamination or sample preparation issue.

As for runs using other samples there is notable Si release in all runs, with the runs without CO₂ showing higher concentrations and, again, this is indicative of dissolution of the glass containers used in the experiments. Like AGH0005 the two runs using AGH0007 with CO₂ do have elevated Si concentrations relative to the comparable blank runs without solid, indicating some contribution from silicate dissolution in these runs.

As for runs using other starting solids, sulphur concentrations are elevated in all runs relative to their solid-free counterparts and, again, likely reflects dissolution of minor sulphate bearing phases present in the samples.

3.3 Discussion

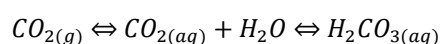
The previous section presented the results from a series of experiments designed to illustrate the possible geochemical effects of injecting hydrogen into a reservoir along with carbon dioxide. Since carbon capture and storage schemes began to receive increased attention in the 1990's a large number of studies have been dedicated to studying the geochemical response of a reservoir to CO₂ injection, while similar studies are now being produced around the concept of hydrogen storage. Fewer studies have been dedicated to understanding the relative geochemical effects, if any, of co-injection of H₂ and CO₂, where, for example, CO₂ can act as the cushion gas with the added benefit of long-term/permanent CO₂ storage in the target reservoir. In order to address this, experiments were run using a small selection of samples using hydrogen alone, carbon dioxide alone, nitrogen alone, and a hydrogen-carbon dioxide mixture, such that the effects of a mixed injection could be compared to those of hydrogen alone. The experiments were carried out at a set of conditions reasonably typical for a depleted hydrocarbon reservoir: at 80°C, 60 bar pressure (though this is likely below usual operating pressures), and with a near-seawater strength (3.5%) NaCl brine.

Due to experimental constraints several aspects of this study should be borne in mind when considering these results. Due to slow leakage, pressure during the experiments generally decreased, sometimes by up to 10 bar over the course of a single run. This will have had the effect of decreasing dissolved gas concentrations in the experiments, which in turn will have influenced the chemistry of the experiments. The overall effect of this would likely be minimal though measurable: a simple PHREEQC calculation suggests that at in-situ conditions a reduction in CO₂ pressure from 60 bar to 50 bar would, for a pure water system, result in an increase in pH from 3.28 to 3.31, for example. Contamination of the experiments, largely through dissolution of the glass containers used, was also an issue, although this was largely mitigated in terms of relative reaction thanks to the control experiments carried out using no solid. It should also be borne in mind that these experiments represent far from equilibrium conditions and that the majority of the reaction observed is due simply to the solid samples reacting with the NaCl fluid, irrespective of the gas phase used. Further, the fraction of the crushed material used was the finest (<325 µm). Use of very fine fractions will generally lead to very rapid dissolution of fine and ultrafine material, generating high levels of reaction/net release, but at rates which would not be comparable to a real-world setting. Conversely, the experiments were not agitated or stirred. This approach simplified the experimental approach/design but does mean that very rapid geochemical interactions (for example calcite dissolution into CO₂ rich fluid) may have become diffusion limited during some of the runs.

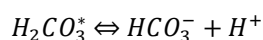
The experiments were designed in this manner in order to provide a set of comparative results for a relatively wide matrix of gas compositions and samples and provide a useful set of data on the relative reaction within various systems, rather than absolute magnitudes or rates of reaction.

The findings for the three different solid samples were broadly similar, despite variations in mineralogy. Across all samples pH of the final fluid was notably lower in the runs using CO₂. pH for runs using CO₂ was broadly comparable, ranging from 6.8 to 7.9, while for runs using H₂ or N₂ only pH covered a higher range from 8.4 to 9.1.

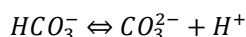
This difference is explained by the initial dissolution of CO₂:



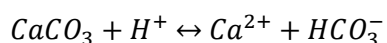
and subsequent generation of acidity through dissociation via:



and:



This generation of acidity will drive mineral dissolution, for example the dissolution of calcite:



And this, in turn, explains the higher net elemental release observed in the experiments using CO_2 relative to those using H_2 or N_2 alone.

Of the elements released through addition of CO_2 , Ca and Mg were the most notable. These were elevated in all experiments using rock samples and CO_2 or CO_2 - H_2 relative to the N_2 and H_2 only runs. There was little difference in Ca/Mg concentrations between runs using CO_2 only or CO_2 - H_2 , while concentrations in runs using rock samples and N_2 or H_2 alone generated concentrations similar to those found for the comparable runs using brine only. These results indicate that carbonate dissolution, driven almost entirely by the addition of CO_2 is a major reaction in these experiments. The presence of H_2 , meanwhile, has little or no impact on the dissolution of carbonates as far as can be deduced from these results. This is of note as several modelling studies have indicated that the storage of H_2 could lead to extensive carbonate dissolution through dissociation of dissolved hydrogen (Bo et al. 2021): these results do not support those findings and are in agreement with the experimental study of (Gelencsér et al. 2023), which indicated that such results may be an artefact of some of the thermodynamic equations/data used in such models.

Potassium was also elevated (relative to brine only runs) across all runs using rock samples. These concentrations are broadly independent on the gas phase used indicating that K release was largely driven by reaction between the solid and the brine (as noted in previous sections possibly driven by ion exchange with the aluminosilicates present in the solid samples (Min, Kim, and Jun 2018)). S concentrations were similarly elevated across all runs using rock samples compared to the brine only controls. Again, this is indicative of reaction between the starting brine and the rock samples, a process largely independent of the reactant gas composition and likely driven by dissolution of minor sulphate phases present in the rock by the brine.

Si concentrations were elevated across all runs and as discussed above the majority of this was likely sourced from the glass containers used. It is notable, however, that concentrations in the hydrogen only runs were higher than those observed for the runs using CO_2 . This difference is likely due to the strong positive correlation between glass solubility and increasing pH above a pH of c. 8 (Strachan 2017). While the contributing phase in this case is glass, the same holds true for amorphous silica in general and for quartz (although the relative reactivity of quartz is considerably less than for amorphous silica). The results here indicate that primary silicate dissolution also contributes to net Si release (increased Si in the rock sample runs relative to their rock-free counterparts), likely through feldspar dissolution, though the contribution from this process is minor relative to the release from glass dissolution for the higher pH runs. Some of this dissolution may have been due to the addition of CO_2 as would be expected under these conditions (e.g. Czernichowski-Lauriol et al. 2006) although there is no direct evidence for this and the primary contributor was likely brine-rock disequilibrium. The results, therefore, highlight three processes which may require consideration when thinking

about CO₂ addition to hydrogen streams generation of lower pH conditions with the addition of CO₂, and dissolution of feldspars under those lower pH conditions. While the release of Si at higher pH is notable in this study, in a reservoir setting the reservoir fluid is at or near equilibrium with quartz in the first instance. Addition of H₂ alone will not increase pH and hence is unlikely to drive additional quartz dissolution and so this process is unlikely to be a major consideration in most systems. Addition of CO₂, on the other hand, while lowering pH, will drive the system away from equilibrium causing Si release through attack of feldspars and other silicate minerals.

Overall, the results presented here correspond to a model where, over short timescales, gas-brine-rock reactions are driven, to a large extent, by CO₂, where it is present. Hydrogen alone does not have a major impact on the geochemical system. Where elemental release has been observed in the experiments presented here it can be attributed (artefacts from glass dissolution aside) either to reaction between the starting brine and the rock samples or to CO₂ induced reaction. Assuming injection of a relatively dry gas stream, the first consideration can be largely ignored, as the formation fluid present will likely be at, or at least relatively close to, equilibrium with the mineral phases present. It is therefore CO₂ induced reactions which will be dominant under reservoir conditions, where CO₂ is included in the gas stream. Under these conditions reactions will likely be similar to those expected during geological sequestration of CO₂: initial acidification of the formation fluid and dissolution of carbonates and (to a lesser extent) aluminosilicate phases followed by, in the longer term, secondary precipitation of carbonates. For a given single injection the overall impact of these reactions may be minimal, as the system will be rapidly buffered back towards equilibrium by dissolution of, e.g., available calcite, but the potential for these reactions to influence a reservoir should be assessed on a site by site basis.

It should be noted that the experiments were carried out under sterilised conditions and the above model considers only abiotic reactions. Where microbes are present, we may expect hydrogen to play a larger role in driving geochemical changes through, for example, changes in redox potential of the fluids present and generation of secondary gases (e.g. CH₄). This would have to be considered on site-specific basis and may require, for example, experiments including specific microbe populations, where they are present (and active) in specific reservoirs.

4 Hydrogen-CH₄ Geochemical experiments

In addition to the hydrogen-carbon dioxide experiments described in the preceding sections, another, smaller, set of experiments were carried out to investigate the potential impacts of including natural gas, consisting of 70-90% methane (CH₄) in hydrogen streams during geological storage. The experiments utilised reservoir sample AGH0005 (see Table 1) and similar experimental conditions to the CO₂ experiments so that the experimental sets remain comparable, but some minor changes were made to the experimental methodology. The changes to methodology and the results of the experiments are presented and discussed below.

4.1 Methodology

As above, AGH0005, a sample of the sandstone reservoir of the Field 1, Hungary, was used in this work. While this is the same as one of the samples used in the CO₂ experiments described in previous Sections, it underwent additional preparation. This involved re-sieving the powdered sample to achieve a coarser and narrower grain size range, 63–180 µm. This fraction was then rinsed with acetone until the supernatant ran clear and left to dry under a fume hood. This process was carried out to remove any ultrafine material likely to give rise to unrealistic reaction and supersaturations.

3.5% NaCl solution was prepared using 99.5% purity NaCl, supplied by Fisher Scientific, a three-point balance, volumetric glassware and deionised water. The starting solution was sampled for measurements of pH, conductivity and a sub-sample for ICP-OES prepared by filtering the solution from a syringed sample through a 0.2 µm nylon syringe filter unit, acidifying with 69% HNO₃ and storing in a fridge prior to analysis. The same sampling procedure was used for the end-run samples. pH and conductivity were measured using a Mettler Toledo SevenExcellence pH meter with an Inlab Micro Pro electrode calibrated prior to use.

The same stainless steel vessels were used as described in Section 3, but rather than using them with stacked glass containers, experiment materials (solids and liquids) were held in Teflon liners partially bored to hold a volume up to 100 ml and holding only one experiment per vessel. This eliminated the contamination by glass dissolution observed in earlier experiments and prevented spillage of one experiment into another during placement or retrieval of the glass containers used previously.

Experiments were started by weighing 10 g of solid into each Teflon Liner followed by 30 ml of the NaCl solution, which had been sparged with nitrogen in order to remove the vast majority of atmospheric oxygen. The liners were then inserted into the steel pressure vessels, which were flushed with nitrogen and sealed. The vessels were then placed in an oven and pressurised to 41 bar with either N₂, CH₄ (as a proxy for natural gas) or a 55.2% hydrogen/methane mixture (all supplied by BOC). The oven was then turned on with a set-point of 80°C. As the vessels warmed the pressure gas pressures applied increased to the target pressure of 50 bar (as per Gay-Lussac's law). The pressure was checked occasionally using an ESI pressure transducer attached to the pressurisation line.

Three experiments were carried out in the manner described above and these are summarised in Table 7.

Table 8: Experimental run summary for CH₄ experiments.

Run ID	Solid	Solid Weight (g)	Temperature (°C)	Average Pressure (bar)	Gas	Starting fluid	Fluid weight (g)	Run Time (days)
1152	AGH0005	10	80	50.0	N ₂	3.5% NaCl	30	14
1153	AGH0005	10	80	50.0	CH ₄	3.5% NaCl	30	14
1154	AGH0005	10	80	50.0	H ₂ /CH ₄	3.5% NaCl	30	14

4.2 Results

Full analytical results from the runs investigating the possible geochemical impacts of the inclusion of methane in hydrogen streams are presented in Table 8, while select elements are shown in Figure 6.

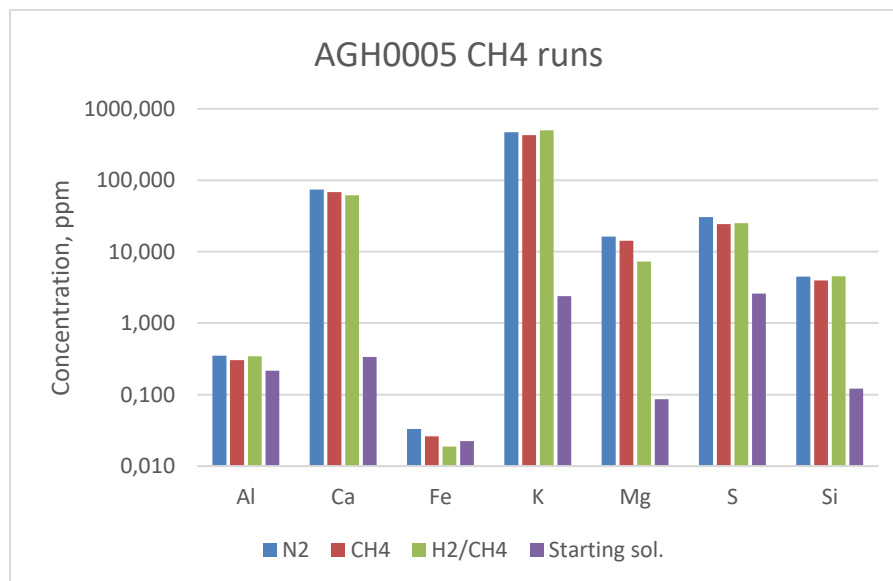


Figure 6: Select elements for CH₄ runs.

The pH and conductivity of the starting fluid are 6.6 and 51 mS/cm, respectively. The pH and conductivities of the reacted fluids, meanwhile, are all elevated relative to the starting fluid but are similar to each other. pH in the reacted fluids ranges from 7.9 to 8.1, while conductivity ranges from 58–59 mS/cm. These values provide a good initial indication that reaction has occurred, and that the reaction is largely independent of the gas used (i.e., impacts of H₂ and CH₄ are minimal).

Table 9: Analytical results for CH₄ runs.

Run	1152	1153	1154	Starting
Gas	N ₂	CH ₄	CH ₄ /H ₂	-
Solid	AGH0005	AGH0005	AGH0005	AGH0005
Final pH	7.88	7.85	8.13	6.64
Final Conductivity (µs/cm)	59115	57545	58262	50791
Analyte	LoD (ppm)	Concentration, ppm		
Ag	0.00022	0.001	BD	BD
Al	0.00512	0.351	0.303	0.344
B	0.00149	0.487	0.424	0.412
Ba	0.00014	0.078	0.082	0.170
Ca	0.00185	74.495	68.040	61.579
Cd	0.00023	BD	BD	BD
Ce	0.00289	BD	BD	BD
Co	0.00020	0.015	0.007	BD
Cr	0.00705	BD	BD	BD
Cu	0.00034	0.038	0.067	0.004
Fe	0.00138	0.033	0.026	0.019
Ga	0.00276	0.023	0.007	BD
Hg	0.00003	0.000	BD	BD
K	0.00195	467.990	429.642	502.184
Mg	0.00025	16.236	14.302	7.312
Mn	0.00005	0.184	0.101	0.071
Na	0.07449	11043	9725	11395
Ni	0.00052	0.229	0.001	0.009
P	0.00339	0.105	0.175	0.236
Pb	0.00367	0.025	BD	0.010
S	0.03738	30.378	24.322	25.073
Si	0.00342	4.464	3.971	4.512
Sr	0.00026	0.516	0.483	0.515
Ti	0.00004	BD	BD	BD
Zn	0.00195	BD	BD	0.002
Zr	0.00195	BD	BD	BD

The minimal influence of the gas phase on the resulting chemistry is confirmed by the elemental chemistry of the end-run samples. In all three runs concentrations of Al, Ca, K, Mg, S and Si are elevated relative to the starting fluid but final concentrations of these elements are near identical across all three runs. The results are indicative of dissolution of primary silicate and carbonate minerals driven entirely by the brine-rock disequilibrium. The addition of CH₄ to the system had little to no observable impact on the system and, likewise, the further addition of hydrogen had no significant effect on the outcome of the experiments.

4.3 Discussion

The previous section presents the results from a small set of experiments designed to investigate the impact natural gas, consisting of 70-90% methane (CH₄) may have on systems where it is injected alongside hydrogen as part of a geological storage scheme. While some

modifications were made to the experimental procedure, conditions were kept largely as for the CO₂ experiments described in the previous section so that the CH₄ experiments so as to provide a complimentary set of results.

The results presented here confirm the finding from the CO₂-hydrogen experiments that hydrogen has little to no impact on the geochemistry of the experimental systems used here: almost all reaction in these runs can be accounted for by disequilibrium between the brine used and the solid samples and this appears to be the driver behind all of the dissolution observed. Unlike CO₂ the addition of CH₄ to the systems had no observable effect in terms of the fluid chemistry.

Similar to the CO₂ experiments discussed in Section 3 of this report, the experimental context of these results should be borne in mind. The brine-rock systems used in these experiments are far from equilibrium and hence experience a relatively large amount of reaction independent of the gas phase used. This reaction may mask more subtle changes driven by the addition of hydrogen or methane. While the experimental design was slightly changed for the CH₄ experiments, to eliminate some contamination issues and the ultrafines present in the CO₂ runs, there remains the issue of agitation. Mixing of the experiments was not possible due to the design of the vessels used and it possible that reactions were retarded or stopped altogether during the runs due simply to lack of agitation.

Bearing the above in mind, the results of these experiments do provide good evidence that significant inorganic reaction involving CH₄ or H₂ is unlikely for the kind of brine-mineral systems represented here. Some more subtle, or mineral specific, reactions may still occur depending on the nature of the storage site. On the basis of these experiments, we would recommend longer term experiments looking at a wider range of likely storage reservoir material, or at individual mineral reaction magnitudes and rates. Ideally such experiments should be carried out at close to equilibrium conditions such that slower, more subtle reactions can be more easily observed (if present).

5 Conclusions and perspectives

This study represents an initial attempt to address the current gaps in knowledge around the likely geochemical behaviour of systems where natural gas, consisting of 70-90% methane (CH₄) or carbon dioxide are used as cushion gases, or are otherwise present, in reservoirs targeted for storage of H₂. The straightforward experimental design employed allowed a large number of experiments to be carried out using select rock samples to assess the relative influence of CO₂ vs H₂ vs CO₂/H₂ and CH₄ vs CH₄/H₂ mixtures on system geochemistry.

The results support the assumption that reaction in such systems will be driven largely by the addition of CO₂ and that the presence of H₂ or CH₄ have relatively little impact on overall geochemistry. While this is true for the experimental systems studied here, it should be noted that in systems where the reducing effect of hydrogen may have a more significant effect on geochemistry (in reservoirs containing significant pyrite, for example) or where redox related reactions may be promoted or catalysed by suitable microbe populations then the presence of hydrogen may exert more of a controlling influence on system geochemistry.

Reactions observed for runs using CO₂ were generally consistent with that expected under CO₂ storage conditions: a lowering of pH as CO₂ dissolves into the brine, followed by significant carbonate dissolution, along with some dissolution or leaching of the feldspars and micas present. For hydrogen-only runs much less reaction was observed and reactions which did occur could largely be attributed either to dissolution of components of the experimental system or to reaction between the brine and solid samples alone (i.e., reactions independent of the gas phase used). Similar to hydrogen, the inclusion of methane in the runs had no discernible effect on the final fluid chemistries.

These results may be viewed as encouraging in terms of the potential storage of hydrogen with CO₂ or CH₄ as cushion gases. The inclusion of CH₄ is likely to have minimal impact on reservoir geochemistry (in terms of abiotic reaction, at least), while the relative reactivity of CO₂ may benefit a storage scheme in terms of trapping of CO₂. In such a system the ideal would be to minimise reaction (i.e. loss of) the stored hydrogen, while promoting CO₂ controlled reactions to encourage long term storage of CO₂ through solubility, and eventually mineral, trapping of injected CO₂ (though the extent to which this is desirable is somewhat dependant on the lifespan of the hydrogen store, the porosity of which operators may not want to reduce significantly while active).

In terms of further work, it is recommended that future experiments take advantage of scanning electron microscope (SEM) and gas chromatograph (GC) analysis in order to better characterise changes to the solid and gas compositions in the system, in addition to characterisation of the reactant brine. Such analysis would help to better characterise reactions in the system and could identify reactions, such as in-situ generation of gases (e.g. H₂S/CH₄) and secondary mineral precipitation (e.g. carbonates) which cannot be determined using the approach of the current work (i.e. from characterisation of a single fluid sample). We also recommend further experiments at closer to equilibrium conditions looking at a wider range of reservoir material or at individual minerals such that a broader picture of hydrogen/methane reactivity can be built, beyond the limited number of samples utilised here.

Care should also be taken in extrapolating these results to, for example, reservoirs with significantly different mineralogy or where biotic processes may exert a larger influence. It is recommended that future experiments should be undertaken with representative populations of microbes, where they may exist, such that their influence in hydrogen mediated redox reactions can be determined. Such reactions may have significant impact on gas and mineral compositions and, as above, such experiments should be complimented with suitable analysis of these phases.

6 References

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