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# D2.5.3
# Modelling of geochemical response to $H_2$ of the Bunter sandstone

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## Abstract

This report was written as part of task 2.5 the ERA-Net ACT funded ELEGANCY project (271498). Part of this task concerns investigating the impact of hydrogen on the microbiology of carbon dioxide storage reservoirs containing gas from hydrogen production. As part of this work geochemical modelling was undertaken in order to inform the experiments. The modelling presented here demonstrates some of the inorganic reaction likely to occur when sandstone core and associated fluid is subject to a $CO_2$-$H_2$ gas pressure. The majority of reaction observed within the modelled systems can be attributed to $CO_2$ dissolution, causing acidification of the solution, and dissolution of several primary minerals in the chosen assemblage: K-feldspar, albite and halite are observed to dissolve under most scenarios, along with some minor quartz precipitation. Major secondary precipitates predicted under $CO_2$ only conditions include dawsonite, barite, and several clay phases (fed mainly through the breakdown of primary feldspars). The addition of $H_2$ gas to the system, in concentrations up to 1% of the total gas pressure, had subtle, but potentially important effects on the solution chemistry: pH remained stable at the value predicted for $CO_2$ only systems, but increasing $H_2$ concentrations suppressed the precipitation of barite and clays, and encouraged the formation of phases such as elemental carbon, witherite and pyrite. Several shortcomings of the approach taken here are identified and will be used to inform future modelling work, and the experimental programme: the available databases are not parameterised for highly saline systems which include $H_2$ gas; the mineral assemblage and solution compositions were assumed, and will be modified according to the experimental programme; the models here are thermodynamic in nature, and take no account of kinetic processes, again, this will be modified as the experimental programme progresses.

# TABLE OF CONTENTS

Page

# 1 INTRODUCTION

In Work Package 2 of the ELEGANCY project, several activities are underway to investigate the physical, chemical and biological properties of the fluid and rock environment of carbon dioxide storage reservoirs and the influence hydrogen will have on them. Amongst these activities are a set of microbiological experiments designed to understand the potential for, and impacts of, hydrogen consuming microorganisms (hydrogenotrophs) in an environment where the stored carbon dioxide includes hydrogen impurities. As well as the organic reactions related to microbe activity, the injection of carbon dioxide and hydrogen into a geological formation will push the geochemical system out of equilibrium, causing changes in the formation fluid, and associated dissolution of minerals, and possible precipitation of secondary phases. It is important that these reactions are properly understood, since they will affect the physical and geochemical properties of the target formation, and may have knock on effects on ongoing microbial processes.

This report describes the creation of a simple geochemical model, using the PHREEQC program, to indicate the likely inorganic geochemical reactions which would occur between injected $CO_2$/$H_2$, the formation fluid, and the formation minerals. This model will be used to inform the initial microbiological experiments, which will take place under in-situ conditions, and will be refined and updated using results from the same, eventually incorporating microbial and kinetic processes.

# 2 MODEL PARAMETERS

## 2.1 Mineralogy

The solid which has been chosen for use in the experimental program is the Bunter Sandstone, now classified as part of the Sherwood Sandstone Group. Specifically, core from appraisal well 42/25d-3 drilled in the Southern North Sea as part of the White Rose project (Metcalfe, Thatcher, Towler, Paulley, & Eng, 2017), will be subsampled. This borehole passed into the Bunter Sandstone at a depth of around 1370 m. unfortunately, at the time of the writing of this report, no mineralogical data was available for the actual samples to be used in the experimental program. As a stop-gap, an equivalent composition was taken from analysis done on the Sherwood Sandstone from a geothermal well drilled onshore in Cleethorpes in 1985 (Busby, 2010). Two samples from the original core were analysed as part of the JouleII project (Holloway et al., 1996), taken from a depth of 1303 – 1307 m. Mineralogical analysis was carried by point counting using a scanning electron microscope (SEM). For the purposes of this work, the average composition from these analyses was simplified, ignoring porosity, as presented in Table 1.

*Table 1 Simplified Sherwood/Bunter sandstone composition used in modelling.*

| Mineral | Quartz | K-Feldspar | Albite | Dolomite | Illite | Clay Matrix/Halite |
|---|---|---|---|---|---|---|
| Weight % | *64* | *17* | *5* | *7* | *3* | *4* |

The mineralogy of this onshore material will have likely been altered via flushing with relatively dilute groundwaters, as compared to the more saline fluids found in formations beneath the Southern North Sea. Hence few evaporitic minerals are found in the samples from the Cleethorpes borehole, while equivalent samples from offshore are likely to have a much higher content in, for instance, halite (Heinemann, Wilkinson, Pickup, Haszeldine, & Cutler, 2012). To address this in this modelling work, the ‘clay matrix’ from the above composition was replaced with the equivalent weight percent of halite in the models. This composition will, of course, be updated for future modelling work, when a specific composition for the experimental material is available.

## 2.2 Fluid Chemistry

While there were analyses carried out on fluids sampled from the Cleethorpes borehole (British Geological Survey, 1985), the fluids sampled were of much lower salinity than those commonly found in the Bunter Sandstone beneath the Southern North Sea (Warren & Smiley, 1994). Therefor two fluid analyses carried out on samples from the Esmond and Forbes oil and gas fields were used to create a more representative composition of the kinds of offshore fluids likely to be encountered in a storage scenario (Warren & Smiley, 1994). The Esmond and Forbes samples were taken from 1936 m and 1792 m depth respectively, within the Bunter Sandstone. The average composition of these two analyses, used in the modelling work presented here, is shown in Table 2.

*Table 2. Fluid composition used in modelling*

| Analyte | pH | Na | K | Mg | Ca | Ba | Fe | Cl | $SO_4$ | $HCO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Value, mol/l | *6.3* | *4.7* | *0.021* | *0.080* | *0.19* | *0.000029* | *0.000029* | *5.4* | *0.013* | *0.00039* |

## 2.3 Model Set-up

All modelling was carried out using the PHREEQC geochemical modelling software (Parkhurst & Appelo, 2013). The model runs were set up so as to mimic the typical conditions of the planned batch-type experiments. In these experiments, a powdered solid is placed in a fluid, and subjected to elevated temperatures and a constant gas pressure.

All model runs were carried out using 30 °C and 80 bar as the simulated temperature/pressure conditions. These conditions would be equivalent to geological storage at depths of around 800 m. A nominal 10 g of solid was simulated in each run, in contact with 500 ml of fluid (compositions given in Tables 1 and 2). Four different gas compositions were used to provide the 80 bar of pressure in the model runs- pure $CO_2$, 99.9% $CO_2$ with 0.1% $H_2$, 99.5% $CO_2$ with 0.5% $H_2$, and 99% $CO_2$ with 1%$H_2$. For each of these gas mixtures, models were run using only the selected fluid, and using the selected fluid and minerals. For both of these two run types (with and without inclusion of minerals), runs were carried out to partial equilibrium (where starting minerals are allowed to dissolve, but secondary minerals are not allowed to precipitate), and full equilibrium (where primary minerals can dissolve, and secondary mineral phases can precipitate). This sequence of model runs is illustrated in Table 3.

*Table 3. Summary of model runs*

| Gas Mix. | *100% $CO_2$* | | | | *99.1% $CO_2$, 0.1% $H_2$* | | | | *99.5% $CO_2$, 0.5% $H_2$* | | | | *99% $CO_2$, 1% $H_2$* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Model Components | *Fluid Only* | | *Fluid and Minerals* | | *Fluid Only* | | *Fluid and Minerals* | | *Fluid Only* | | *Fluid and Minerals* | | *Fluid Only* | | *Fluid and Minerals* | |
| Secondary Phases | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** | ***Y*** | ***N*** |

It should be noted that, as it has been used here, PHREEQC predicts equilibrium conditions, i.e. the rates of reactions have not been taken into account. In many natural systems and experimental systems, true equilibrium is never reached. The modelling presented here, therefor, is useful in predicting the direction of reactions, and which mineral phases are likely to dissolve or precipitate, but is not a guide to the absolute magnitude of reaction to be expected in the actual experiments. Another factor which will affect the magnitude of reaction observed is the fluid:rock ratio. Here a nominal 50:1 ratio has been chosen, but this may vary in the actual experimental runs.

The Lawrence Livermore National Laboratory database (llnl.dat) was used with PHREEQC for the purpose of this modelling. This database was used as it provides consistent thermodynamic data for a wide variety of phases and species. The notable shortcoming of this database, in terms of the model runs presented here, is that it is not designed to use with fluids of high ionic strength. At high concentrations, components of high ionic strength fluids (such as chloride brines, as modelled here), can interfere with each other, affecting their activity in the fluid, and hence the thermodynamics of the system as a whole. The common approach to this problem is to account for these additional ionic interactions by correction using measured ‘Pitzer parameters’. Unfortunately these interaction parameters are available only for a limited number of species. The Pitzer and FREZCHEM databases (pitzer.dat and frezchem.dat) supplied with PHREEQC, both of which can be used for modelling of high ionic strength fluids, do not include parameters for $H_2$ gas, for example, making them unusable for this work. The inability of the models to account for these interactions introduces an additional uncertainty into the results presented here, and should be kept in mind.

# 3 MODEL RESULTS

## 3.1 Fluid-gas only model runs

Initial model runs were carried out using only the selected fluid and the various gas pressures presented in Table 3. These runs serve to illustrate the effects of gas pressure alone, ignoring any mineral input. Eight runs in total were carried out using this set-up, two for each selected gas mixture: with and without mineral precipitation included. An additional model was also run using only the fluid, with no gas mixture or minerals, in order to check that stability of the selected composition at the model temperature/pressure conditions. Model results are summarised in Table 4, at the end of this section.

### 3.1.1 Starting Fluid

Modelling of the selected fluid composition indicates that it is close to equilibrium at the model conditions of 30°C and 80 bar. The solution is close to charge balanced, with a percent error of only -1.71. Partial equilibrium modelling of the solution indicates that it is slightly oversaturated with respect to barite ($BaSO_4$), goethite (FeOOH), hematite ($Fe_2O_3$) and magnetite ($FeSO_4$) at the selected conditions. If taken to full equilibrium the model predicts that pH will remain stable, with a starting and final value of 6.3, and that of the oversaturated phases, only barite and hematite are likely to precipitate, and in very small amounts (6E-3 g/l of barite and 3E-6 g/l of hematite). At full equilibrium the fluid is predicted to be slightly reducing, with an Eh of -22 mV.

### 3.1.2 100% $CO_2$

Under 80 bar $CO_2$ pressure, the pH of the fluid drops from 6.3 to 2.8 at full equilibrium, as acidity is generated through dissolution of $CO_2$ and no minerals are available for extra buffering. Under these conditions the model predicts small amounts (6E-4 g/l) of barite precipitation, and the fluid having being relatively oxidising, with an Eh of 478 mV.

### 3.1.3 99.9% $CO_2$ + 0.1% $H_2$

Under the 99.9% $CO_2$ – 0.1% $H_2$ gas mixture, pH is predicted to drop from 6.3 to 3.6 under full equilibrium conditions. The final pH is slightly higher than that predicted for the $CO_2$ only model above. This is apparently due to various changes in speciation brought about by the addition of hydrogen, including uptake of some hydrogen into methane molecules, and increases in bicarbonate and hydroxide concentrations. At partial equilibrium barite, pyrite ($FeS_2$) and elemental sulphur (S) are predicted to be oversaturated. Small amounts (4E-4, 3E-4, and 3E-2 g/l respectively) of these phases are predicted to precipitate at full equilibrium. Under these conditions the fluid is predicted to be slightly oxidising, with an Eh of 25 mV.

### 3.1.4 99.5% $CO_2$ + 0.5% $H_2$

Under the 99.5% $CO_2$ – 0.5% $H_2$ gas mixture, pH is predicted to drop from 6.3 to 3.6 under full equilibrium conditions. The additional hydrogen in this model compared to the 0.1% $H_2$ model causes very little difference in the pH value attained. Differences do occur in terms of the overall equilibrium of the system however. Under these conditions the fluid at partial equilibrium is oversaturated in elemental carbon and pyrite, while barite and elemental sulphur remain undersaturated. At full equilibrium both elemental carbon and pyrite are predicted to precipitate

(9E-2 and 3E-4 g/l respectively). The fluid under these conditions is, as for the system with 0.1% $H_2$, predicted to be slightly oxidising, with an Eh of 21 mV.

### 3.1.5 99% $CO_2$ + 1% $H_2$

Under the 99% $CO_2$ – 1% $H_2$ gas mixture, as for the other hydrogen mixtures used above, pH is predicted to drop from 6.3 to 3.6. As for the 0.5% $H_2$ model run, pyrite and elemental carbon are predicted to be oversaturated at partial equilibrium and to precipitate, in slightly larger amounts (2E-1 and 3E-4 g/l respectively), at full equilibrium. In addition the model predicts the formation and oversaturation of methane at partial equilibrium conditions, though at full equilibrium this is brought back to undersaturation via the precipitation of elemental carbon. While any volumes of methane formed are likely to be very low, the results suggest that gas generation during experimental runs may be something to take into consideration. At full equilibrium the fluid in this system is again predicted to be slightly oxidising, with an Eh of 22 mV.

*Table 4. Summary of fluid-gas only model runs*

| Gas Mixture | Equilibrium pH | Equilibrium Eh (mV) | Predicted oversaturated phases | Predicted precipitates | Effect on starting minerals | |
|---|---|---|---|---|---|---|
| | | | | | Dissolve | Precipitate |
| No gas | *6.30* | *-22* | *Barite, Goethite, Hematite, Magnetite* | *Barite, Hematite* | *N/A* | *N/A* |
| 100% $CO_2$ | *2.78* | *478* | *Barite* | *Barite* | *N/A* | *N/A* |
| 99.9% $CO_2$, 0.1% $H_2$ | *3.62* | *25* | *Barite, Pyrite, Elemental Sulphur* | *Pyrite, Elemental Sulphur* | *N/A* | *N/A* |
| 99.5% $CO_2$, 0.5% $H_2$ | *3.57* | *21* | *Elemental carbon, Methane, Pyrite* | *Elemental Carbon, Pyrite* | *N/A* | *N/A* |
| 99% $CO_2$, 1% $H_2$ | *3.57* | *22* | *Elemental Carbon, Methane, Pyrite* | *Elemental Carbon, Pyrite* | *N/A* | *N/A* |

## 3.2 Fluid-gas-mineral models

Final model runs were carried out using selected mineral and fluid compositions and, as for the fluid only models, were run to partial and full equilibrium. These model runs provide the best indication of the direction of reactions likely to occur in the actual experimental runs, though, as noted in Section 2, the absolute magnitudes of reaction observed in these runs will not match those likely to be achieved in the experiments. An additional model was also run using only the selected fluid and minerals at the same pressure temperature conditions (i.e. no reactive gas phase was included). Model results are summarised in Table 5, at the end of this section.

### 3.2.1 Gas free

In the model run using no reactive gas phase (reacting only the selected fluid and minerals), pH was predicted to rise slightly from 6.30 to 6.32 at full equilibrium conditions. At full equilibrium conditions, of the starting minerals, quartz is predicted to precipitate, while K-feldspar, albite, illite, and halite are predicted to dissolve. Within the model dolomite is predicted to dissolve and reprecipitate as the more stable ‘ordered’ dolomite, though this is considered unlikely under experimental conditions. Secondary phases predicted to form in small amounts include various clays and zeolites, as would be expected following the breakdown of feldspars, muscovite, and barite. At full equilibrium the system is predicted to be slightly reducing, with an Eh of -70 mV. This model illustrates that the fluid-mineral system chosen, at the selected pressure and temperature conditions, is not in equilibrium, and that preconditioning or tweaking of the experimental fluid may be required prior to batch experiments.

### 3.2.2 100% $CO_2$

Under 100% $CO_2$ conditions, the fluid pH dropped from 6.3 to 4.4 at full equilibrium, notably higher than the pH of 3.6 predicted for the equivalent mineral free system. As seen in the gas free model above, K-feldspar, albite, dolomite, illite and halite are all predicted to dissolve under these conditions, though in considerably higher quantities, due to the increased acidity of the system. As for the gas free system described above, small amount of quartz (most likely as amorphous silica) is predicted to precipitate. At partial equilibrium a large number of phases are predicted to be oversaturated, including alunite ($KAl_3(OH)_6(SO_4)_2$), barite, dawsonite ($NaAlCO_3(OH)_2$), diaspore ($AlHO_2$), gibbsite ($Al(OH)_3$), goethite, hematite, kaolinite ($Al_2Si_2O_5(OH)_4$, and various clays phases (largely beidellites and nontronites). Of these, barite and dawsonite are the only phases predicted to precipitate in notable quantities (6E-4 and 1.4 g/l respectively). It should be noted that while dawsonite is often predicted to precipitate as a secondary phase in $CO_2$ rich environments, it is rarely observed in such systems in nature (Wilkinson et al., 2009). At full equilibrium the system is predicted to be relatively oxidising, with an Eh of 330 mV.

### 3.2.3 99.9% $CO_2$ + 0.1% $H_2$

The addition of 0.1% $H_2$ makes little difference to the pH drop observed in system, with the pH at full equilibrium being 4.4, as for the pure $CO_2$ system described above. As for the other modelled systems described in this section, K-feldspar, albite, illite and halite are all predicted to dissolve under these conditions, with small amounts of quartz precipitating. The oversaturated phases predicted at partial equilibrium conditions are largely as for the 100% $CO_2$ system described above, with the notable additions of elemental carbon and sulphur, witherite ($BaCO_3$) and pyrite. Of these small amounts of barite (6E-4 g/l), elemental carbon (4E-5 g/l), and pyrite (3E-4 g/l), and larger amounts of dawsonite (1.4 g/l) are predicted to precipitate under full equilibrium conditions. While the barite and dawsonite precipitation is largely the same as observed for the pure $CO_2$ system, we can attribute the increased saturation of elemental carbon and sulphur, and pyrite to the addition of hydrogen. At full equilibrium the system is predicted to be relatively reducing, with an Eh of -272 mV.

### 3.2.4 99.5% $CO_2$ + 0.5% $H_2$

Again, the extra hydrogen available in the 0.5% $H_2$ model makes no difference to the pH of the fluid at full equilibrium conditions, with the same drop to pH 4.4 as observed for the systems above. Of the starting minerals K-feldspar, albite and halite are predicted to dissolve, while small amounts of quartz and illite are predicted to precipitate. At partial equilibrium the phases predicted to be oversaturated are largely as for the 0.1% $H_2$ system described above, though elemental sulphur is undersaturated and methane is oversaturated, again suggesting that methane generation may be something to watch for during the experiments. At full equilibrium small amounts of pyrite (3E-4 g/l) and witherite (3E-4 g/l) are predicted to precipitate, with larger amounts of elemental carbon (0.1 g/l) and dawsonite (1.4 g/l), indicating that the increase in $H_2$ gas, from 0.1 to 0.5 %, lead to increases in the precipitation of elemental carbon and witherite. The system is predicted to be slightly reducing at full equilibrium, with an Eh of -27 mV.

### 3.2.5 99% $CO_2$ + 1% $H_2$

As for the other gas systems modelled in this section, at full equilibrium the 1% $H_2$ system shows a drop in fluid pH from 6.3 to 4.4. As for the 0.5% $H_2$ system, of the starting minerals K-feldspar, albite and halite are predicted to dissolve, while some quartz and illite precipitation is observed. At partial equilibrium the phases predicted to be oversaturated are as observed for the 0.5% $H_2$ gas system described above. The precipitates predicted at full equilibrium are also near identical: elemental carbon (0.2 g/l), dawsonite (1.4 g/l), pyrite (3E-4 g/l), and witherite (3E-4 g/l). The only difference in precipitates caused by the increase in $H_2$ concentration, therefore, was an increase in elemental carbon precipitate. At full equilibrium the system is predicted to be slightly reducing, with an Eh of -27 mV.

*Table 5. Summary of fluid-gas-mineral model runs*

| Gas Mixture | Equilibrium pH | Equilibrium Eh (mV) | Predicted oversaturated phases | Predicted precipitates | Effect on starting minerals | |
|---|---|---|---|---|---|---|
| | | | | | Dissolve | Precipitate |
| No gas | *6.32* | *-70* | *Barite, Beidellite, Boehmite, Cronstedtite, Dawsonite, Diaspore, Goethite, Hematite, Kaolinite, Magnetite, Mesolite, Montmorillonite, Muscovite, Nontronite, Paragonite, Stilbite, Witherite* | *Barite, Mesolite, Muscovite, Nontronite* | *K-feldspar, Albite, Dolomite, Illite, Halite* | *Quartz* |
| 100% $CO_2$ | *4.39* | *330* | *Alunite, Barite, Beidellite, Boehmite, Dawsonite, Diaspore, Gibbsite, Goethite, Hematite, Kaolinite, Muscovite, Nontronite, Paragonite, Pyrophyllite, Witherite* | *Barite, Dawsonite, Nontronite* | *K-feldspar, Albite, Dolomite, Illite, Halite* | *Quartz* |
| 99.9% $CO_2$, 0.1% $H_2$ | *4.39* | *-272* | *Alunite, Barite, Beidellite, Boehmite, Elemental Carbon, Dawsonite, Diaspore, Gibbsite, Kaolinite, Muscovite, Paragonite, Pyrite, Pyrophyllite, Elemental Sulphur, Witherite* | *Barite, Elemental Carbon, Dawsonite, Pyrite* | *K-feldspar, Albite, Dolomite, Illite, Halite* | *Quartz* |
| 99.5% $CO_2$, 0.5% $H_2$ | *4.40* | *-27* | *Beidxellite, Elemental Carbon, Dawsonite, Diaspore, Gibbsite, Kaolinite, Muscovite, Paragonite, Pyrite, Pyrophyllite, Witherite, Methane* | *Elemental Carbon, Dawsonite, Pyrite, Witherite* | *K-feldspar, Albite, Dolomite, Halite* | *Quartz, Illite* |
| 99% $CO_2$, 1% $H_2$ | *4.40* | *-27* | *Beidellite, Boehmite, Elemental Carbon, Dawsonite, Diaspore, Gibbsite, Kaolinite, Muscovite, Paragonite, Pyrite, Pyrophyllite, Witherite* | *Elemental Carbon, Dawsonite, Pyrite, Witherite* | *K-feldspar, Albite, Dolomite, Halite* | *Quartz, Illite* |

# 4 CONCLUSIONS, SUMMARY AND FUTURE WORK

## 4.1 Modelling parameters and set-up

The models described in the preceding sections were set-up using assumed compositions and conditions. There are several factors which should be considered when assessing the validity and utility of these models, and these in turn illustrate some considerations which should be made in the experimental work and any further modelling:

- It has been assumed that the Endurance sandstone core from the Southern North Sea to be used in the experiments is equivalent in composition to onshore Sherwood Sandstone samples taken from near equivalent depth, with the addition of minor halite, which may have been dissolved by flushing of relatively dilute groundwaters. This assumption is largely reasonable- the major components of the offshore material are likely to be similar, though quantities of dolomite or halite, for example, may vary considerably from the values used here. This issue can easily be addressed in future modelling work, by editing the model parameters once an accurate composition of the experimental material is known.

- It has been assumed that the fluid composition to be used in the experiments is roughly equivalent to the average composition found in the sandstones of the Southern North Sea. This assumption is problematic. It is known that fluid compositions can vary widely from well to well (Warren & Smiley, 1994), even within the same formation. Additionally, it has been demonstrated here that the chosen fluid composition was far from equilibrium with respect to the chosen mineral assemblage (see Section 3.2.1). This suggests some care should be taken in choice of experimental fluid composition, in order to avoid far from equilibrium effects induced by the fluid alone (i.e. mineral dissolution). In terms of future modelling work, the issue of an assumed composition (along with experimental pressure and temperature conditions) will obviously be negated once the conditions of the experimental programme have been finalised.

- The other major issues with the modelling presented here is the high salinity of the fluids. Most thermodynamic models are generally parameterised for work below salinities of, perhaps, 0.5 M. Depending on the composition of the brine being dealt with, they may produce reasonably reliable results up to salinities of 1 M. The brine composition used here, based on samples from the sandstones of the Southern North Sea, has a salinity of around 5 M. As discussed in Section 2, this would usually be dealt with by using a database specifically parameterised for use at high salinities, such as the Pitzer of FREZCHEM databases. However, neither of these databases include data for $H_2$ gas, making of less utility in this work. Without experimental results it is unclear what effect the high salinity of the fluids has had on the results presented here, although future modelling work can assess this by simply modelling $H_2$ free systems using the Pitzer or FREZCHEM databases, and comparing the results to those produced by the LLNL database. Enhancing these databases with the data required would be a major task, and beyond the scope of this project. It may be that the experimental programme uses a less saline fluid, in which case this would no longer be an issue.

- The models presented here are purely thermodynamic and ignore any kinetic effects. The rates of reaction will have a considerable effect on the chemistry observed within the experimental systems, and it will be of utility to introduce dissolution and precipitation kinetics into future models, as experimental parameters (solid mineralogy etc.) are finalised.

In summary, while the modelling presented here is useful as a means of highlighting some potential issues with the proposed experimental systems, it will be significantly enhanced by the finalisation of experimental parameters and compositions, and will be further enhanced when experimental results are available for validation and comparison.

## 4.2 Model results

The models presented here were designed primarily to give some insight into the inorganic processes likely to occur during experiments investigating $CO_2$ with $H_2$ storage in sandstones.

The conclusions from this modelling work, which will inform the experimental and further modelling work going forward are:

- While the initial fluid chemistry is stable, the selected fluid-mineral combination is not in equilibrium, causing dissolution of K-feldspar, albite, illite, and halite from the primary mineral assemblage. Quartz is predicted to precipitate, while the model ‘dolomite’ is predicted to dissolve and reprecipitate as a more stable secondary dolomite. This result suggests that further thought should be given to the fluid chemistry prior to the running of experiments to avoid far from equilibrium effects.

- In terms of reaction observed under gas pressure, most reaction was due to the $CO_2$ present, with the addition of $H_2$ making small, though potentially important, changes to the system chemistry. Initial dissolution of $CO_2$ causes large scale dissolution of primary minerals, due to acidification of the model fluid. In most cases K-feldspar, albite, illite, and halite are predicted to dissolve, with some minor quartz precipitation. The dissolution of primary feldspars leads to oversaturation with respect to several clay phases, which are predicted to precipitate along with phases such as barite and dawsonite.

- While the addition of $H_2$ gas has little effect on the broad solution chemistry, as indicated by the stable pH values across all models, the results do suggests that the addition of $H_2$ suppresses the formation of barite and the clay phases, and leads to predicted precipitation of elemental carbon, pyrite, and witherite, alongside the dawsonite precipitates predicted due to the $CO_2$ pressure. Higher concentrations of $H_2$ also encourage the precipitation of illite, in addition to the quartz predicted to precipitate in the $CO_2$ only models.

- Redox conditions are difficult to predict accurately without detailed a chemistry of the systems being modelled, but the modelling broadly indicates that addition of $H_2$ to these systems will take them from relatively oxidising conditions (under $CO_2$ only conditions), to slightly reducing (for the majority of fluid-mineral systems modelled including $H_2$).

- Some of the model runs also predict fluid oversaturation with respect to methane. While any volumes formed are likely to be metastable and small, it will be worth bearing in mind the potential for gas generation during the experimental runs.

In summary, the modelling results suggest that under a $CO_2$-$H_2$ atmosphere widespread dissolution of primary minerals will occur, largely due to the $CO_2$ present, followed by secondary precipitation of clays, carbonates (such as dawsonite), and pyrite. There is also the possibility of secondary gas generation.

## 4.3 Future Work

The modelling work presented here will be built upon as the experimental programme moves forward. Initial changes will involve updating the solid and fluid compositions as these become available for the materials to be used in experiments. This, in turn, will allow the inclusion of detailed kinetics for individual mineral phases, allowing the timing of reactions to be considered more carefully. The issue of modelling highly saline fluids may also need to be addressed, initially through simple comparative modelling to scope out the likely impact of these effects on the results. Further work will be carried out to tie the inorganic reactions modelled here, to the microbial effects the laboratory experiments are designed to observe.

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