

ANLEC Project 3-1110-0101: Review of laboratory-scale geochemical and geomechanical experiments simulating geosequestration of CO₂ in sandstone, and associated modelling studies

G. K. W. Dawson^a, H. Sidiq^b, J. Pearce^{a,d}, J-F. Gao^a, S. D. Golding^a, V. Rudolph^b, Q. Li^c and H. Xing^a

^a School of Earth Sciences, The University of Queensland, QLD 4072, Australia

^b School of Chemical Engineering, The University of Queensland, QLD 4072, Australia

^c School of Engineering, Griffith University, QLD 4111, Australia

^d CO2CRC, GPO Box 463, Canberra, ACT 2601, Australia

E-mail addresses: g.dawson@uq.edu.au (G.K.W. Dawson); s.golding1@uq.edu.au (S.D. Golding)

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Executive Summary

This review focuses on geomechanical and geochemical experiments and associated models reported in the literature relevant to geosequestration of CO₂ in sandstone, supporting ANLEC Project 3-1110-0101.

This project encompasses three key parts, aimed at supporting CO₂ geosequestration field demonstration/commercial projects: Part 1, geochemical reaction investigations of the CO₂-H₂O-rock system of target host formations, identifying changes to mineralogy, porosity and permeability; Part 2, measurements of 3D mechanical properties and 3D/4D permeability, investigating their dynamic changes over reaction time; Part 3, advancing development of physical and numerical models, to replicate the lab findings of fluid and mass transport, for application at different spatial and temporal scales.

Laboratory experiments will be conducted on cores from the target formations of the Wandoan Power CCS project in Queensland and the South West CO₂ Geosequestration Hub in Western Australia (through an exchange with Curtin University/CSIRO projects also funded by ANLEC). Additionally, our team is collaborating with an ANU/CTSCo-led ANLEC project that will further characterise the Wandoan cores with high-energy CT scanning.

Geochemical changes in the reservoir occur as a result of disturbance to the subsurface conditions and chemistry during CO₂ injection and storage. The position and dimensions of the acidic region of the water-CO₂ mixing front, where the changes are relatively fast, shift over time with plume migration, which in turn causes dehydration around the injection well that may result in salt precipitation. Over a longer time frame, further chemical alteration within the wider reservoir occurs as a result of slower dissolution and precipitation reactions. In the literature these various reactions have been examined either as simple (single mineral – well defined fluid) or mixed (mixed minerals and complex fluids, including highly saline solutions) systems.

Most lab-scale geochemistry studies have used batch reactors, which rely on soaking solid samples over extended periods and then examining the changes to the fluid and/or the solid material. A smaller number of studies have used continuous flow reactors. In both cases, outcomes with respect to observed mineralogy changes have been mixed, mainly corresponding to the complexity of the system being probed. Fluid phase permeability is specific to a given porous medium, and is correlated with features such as pore geometry, porosity, tortuosity and specific surface area. These, as well as the strength and elastic properties for a given rock also change dynamically on both short and long timescales, in ways which are poorly understood. In particular, for CO₂ sequestration, there are at least two fluid phases (water saturated with CO₂ and CO₂ fluid saturated with water) and these interact with each other and with the rock material in ways still poorly understood. The relationship between 3D stresses and rock strength following chemical and physical alteration, and their dynamic and directional evolution is also poorly constrained.

Many previous geochemistry studies have used various computer programs based on principles of thermodynamics or mass transport to model chemical equilibrium under new transient conditions after a disturbance, and some even incorporate chemical kinetics. Only a small number of experimental studies have actually determined parameters such as reaction rate constants for minerals reacting with carbonic acid, with most if not all data included in databases generally used by modelling software having been determined for systems that did not contain carbon dioxide. Often the stock databases are quite limited in terms of applicability to sequestration conditions, as the water-mineral interaction parameters used are often only available for conditions at 25°C and one atmosphere pressure and must be extrapolated to other conditions. Alternatively, data measured for other conditions can be manually imported into the modelling program database, but as mentioned already, directly applicable data may still not be available. Some programs include multiphase fluid behaviour and transport, with various degrees of integration of multi-physics coupling.

While out of the current scope of this project, real flue gases will contain small amounts of the co-contaminants SO_x , NO_x and O_2 , which form stronger acids than carbonic acid, and their effects are very poorly constrained.

The main gap which will be addressed by our project is the lack of *integrated* studies assessing *both* the geochemical and physical changes to the same target rocks and fluids occurring during CO_2 sequestration in sandstone, both experimentally in the short term and longer term by modelling.

1. Introduction

1.1. Rationale for review

The current project is centred on two main research concerns related to CO_2 injection aspects of CCS in deep sandstone formations.

The first theme considers the chemical interactions between rock-water-injected CO_2 . The principle hypothesis is that that carbonic acid, arising from the injected CO_2 interacting with the subsurface water, will dissolve minerals in the near-wellbore region, causing an increase in porosity and accessibility of more pore space. This would have the desirable outcome of an increase in permeability, which is a key determinant of fluid injectivity (cf. Gunter et al., 2008; Massarotto et al., 2010).

The mixing zone between the injected CO_2 and the formation water gradually moves radially outwards from the injection well. Behind the mixing zone, the fluid is predominantly CO_2 which dries out the local environment, and ahead of it is predominantly formation water. The water chemistry may be fresh or saline. Areas dominated by CO_2 containing dissolved water could have precipitation of minerals such as salts, and so desiccated parts of the reservoir may experience permeability reductions due to salts occluding pores (Bacci et al., 2011; Muller et al., 2009; Pruess, 2005). In the mixing zone, the environment is expected to be acidic (from \sim pH 3.0 up to near-neutral), comprising CO_2 saturated water. We consequently focus attention in this project on systems under the influence of high CO_2 pressures. This affects both mechanical and chemical behaviour of the subsurface solids.

The second theme of the project investigates whether the process of injecting supercritical CO_2 into sandstone rock may lead to structural changes in the formation. High disposal rates may require that the injection pressure that drives fluid flow be higher than the 'natural' reservoir pressure, causing substantial near-well stress increases and formation overpressure. These effects are greatest in the near wellbore region where the flows are the highest.

Changes in permeability experienced in this area have a great effect upon injectivity. Changes to permeability in the far-field has a lower impact on injectivity because the flow is much more dispersed, but are still important for life-of-field CO_2 plume behaviour.

1.2. Overview of review

This review seeks to provide an examination of the state of knowledge of laboratory scale geochemistry and geomechanics for CO_2 geosequestration in sandstone reservoirs. It starts with a review of CO_2 behaviour under conditions relevant to geosequestration. Understanding geochemical and geomechanical aspects of geosequestration requires separating many different physical and chemical processes that occur simultaneously, and this is most conveniently done using well controlled laboratory-scale experiments. These take many forms, and reside in the literature of many discipline areas. The small-scale investigations are framed by or provide input to mathematical models at a variety of scales, and this connection is also reviewed.

1.3. CO₂ geochemical and geomechanical behaviour under geosequestration conditions

Part 1 of the project will investigate the complex reactions of CO₂-water-rock as a function of temperature, pressure, and water salinity. It targets clastic reservoirs with and without carbonate cements, for geosequestration of CO₂ in the Wandoan Power CC&S Project in Queensland.

Commonly for deep (>800m) formations, CO₂ will be injected above the supercritical pressure into water saturated formations. In the latter case, the injected fluid either compresses the water or rock material in the reservoir that consequently has a very limited capacity, or displaces water that consequently must move into adjacent pore space. Pressure management schemes can be used to reduce pressure-related constraints on storage capacity and typically involve extraction of formation water from storage formations and re-injection into overlying or underlying formations.

Various equations of state, such as the cubic Stryjek-Vera second modification of the Peng-Robinson equation (Stryjek and Vera, 1986) can successfully predict the density of pure CO₂ over all temperature and pressure conditions relevant to geosequestration, from pipeline to reservoir conditions (Dawson, 2012). However, the density of mixed CO₂ and brine is more difficult to model. CO₂ density is a major control upon plume migration potential, and is strongly phase dependent.

If injected CO₂ has a different temperature from the subsurface at the injection point, a temperature gradient around the well-bore will exist, in addition to the density gradient. This has implications for CO₂ solubility and therefore acidity of mixed CO₂-water in the near well-bore region. Cold liquid and supercritical CO₂ have also been observed to fracture rock (Ishida et al., 2012).

The plume front, which advances through the storage volume as more fluid is injected, grades from water through mixed CO₂/water to pure CO₂. Carbon dioxide has a complex interaction with water. Spycher et al. (2003) and Spycher and Pruess (2005) tabulated CO₂-water mutual solubility over a range of temperatures and pressures, for fresh water and brines respectively. Temperature, pressure, and salinity all affect CO₂ solubility. Carbonic acid forms in the presence of high partial pressures of CO₂, whereas alkaline bicarbonate and/or carbonate anions are formed under lower partial pressures of CO₂.

Major controls over the pH of carbonic acid are CO₂ partial pressure, the presence/absence of buffering anions in solution, and the value of the first ionisation constant of carbonic acid, which is dependent upon both temperature and pressure. Values for this constant have been experimentally determined and tabulated for a range of pressures and temperatures relevant to CO₂ geo-sequestration. Overall, the first ionisation constant decreases in value with temperature but increases with pressure (Read, 1975).

Dissolution of mineral matter occurs as a result of reactions between SC-CO₂, rock and water. The CO₂ at reservoir conditions will often be above its critical point of 31.1°C and 7.38 MPa; these conditions occur at depths generally below ~800 m at Queensland conditions, using a geothermal gradient of 1.82 °C/100 m and a mean annual surface temperature of 25°C (Massarotto et al., 2010).

As the injected CO₂ displaces water, a mixing front of variable dimension is created. It may be expected that most of the geochemical reactions associated with injection of supercritical CO₂ (SC-CO₂), or liquid or gaseous CO₂, take place at the mixing front, where carbonic acid will be formed, which will lead to dissolution of mineral matter.

The position and dimensions of acidic and alkaline regions of the water-CO₂ mixing front shift over time as the plume increases in volume and migrates through the reservoir. CO₂ in the supercritical state is largely immiscible with water (cf. Law and Bachu, 1996) and acts to displace formation water. Further drying out of residual moisture within rocks occurs as (fresh) dry SC-CO₂ passes through reservoir zones and picks up moisture by dissolution.

Minerals dissolved in the acidic conditions that occur at the mixing front are transported by flow and diffusion dispersing throughout the reservoir. The extent of mineral dissolution/precipitation will depend on the spatial distribution and nature of the minerals present and the original composition of the formation brines.

2. Lab-scale studies

2.1. Laboratory geochemical studies

The results of experiments with rocks and carbonic acid are often sample specific, and so Gaus (2010) reasoned that such experiments are of only limited value in comparison to determining the reaction rates of individual minerals.

It may also be argued that the behaviour of individual minerals exposed to carbonic acid, whilst important, is not necessarily indicative of whole rock behaviour, especially given that some reactive minerals present in the rock may never encounter carbonic acid due to isolation from flow pathways through the rock and shielding by less-reactive surrounding minerals. Even if exposed, mineral dissolution is dependent upon a number of factors including reactive surface area available to reagents, impurities present within minerals, and mass transfer to/from the site of interaction between fluid and mineral.

Alteration of cements, matrix and reactive clasts may either enhance or block porosity and hence modify permeability over time, depending upon which phases react and which (if any) are precipitated. In addition, these changes may cause local compression or dilation due to changes in composition. Therefore, only by experimenting upon representative whole rock samples of target formations can the reactive behaviour of a reservoir be holistically examined, and realistic data be fed into models.

Numerous geosequestration laboratory-scale experiments have been performed, summarised in Table 1. The pertinent findings of the studies focused upon here were predominantly for sandstones containing various minerals. The studies incorporated a variety of sample characterisation and fluid analysis techniques; some have also included a component of modelling (Table 2).

The studies follow two main experimental procedures: batch-soak studies and continuous flow-through experiments. In batch experiments, a block of material (e.g. sandstone) is soaked in a fluid (e.g. water-CO₂) under set conditions. The fluid is sampled at set intervals for analysis. At the end of the experiment, the solid is also retrieved and examined. In a continuous experiment, the fluid is passed over or through the sample. The fluid may be analysed continuously and the solid sample is generally retrieved and examined after the end of the experiment.

The major differences between the procedures are:

- Reaction stoichiometry. In batch testing the fluid is defined by its composition and initial quantity. In flow-through systems this is defined by the fluid composition and flow rate.
- Residence time. In batch reactions this is determined by how long a vessel is held at a given temperature and pressure. In flow-through systems this is determined by the bulk flow rate relative to the volume of the reactor.
- Equilibrium. In batch systems the system equilibrates according to the initial stoichiometry (proportions) of the fluid and solid. In flow through systems, the fluid is constantly replenished and may be recirculated (mimicking the batch stoichiometry) or constantly refreshed.
- Exposure. In batch systems, the solution is transported into and out of the solid sample pore space by (slow) diffusion processes. In flow through systems, this can be managed so that viscous flow occurs through the sample pore space. This greatly reduces the experiment time.

2.1.1. Batch-soak reactor studies

Most of the studies have used batch reactor-type set-ups (e.g. Figure 1), with only a few of the experiments utilising continuous-flow reactors (cf. Shi et al., 2011; Shiraki and Dunn, 2000). Part of the reason for this is the difficulty in detecting dissolved ions resulting from interaction with alumina-silicate and other minerals in continuous flow reactor outlet fluids, due to their generally very low concentration having only been in contact with the sample for a limited time.

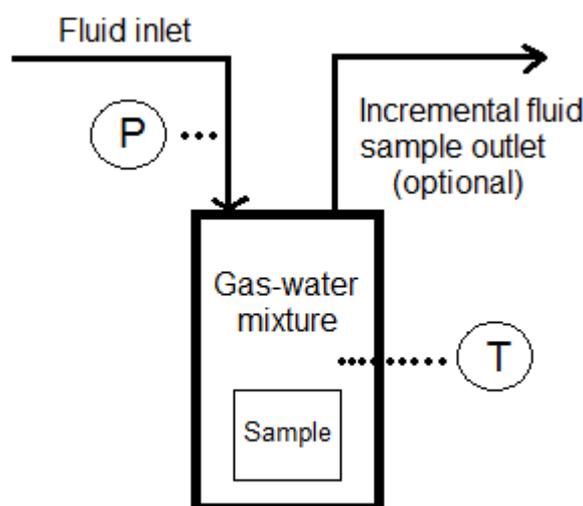


Figure 1: Basic concept of geochemical batch reactor

An early batch reactor study, Gunter et al. (1997), found no significant change in mineralogy after month-long experiments with powdered samples of a glauconitic sandstone in an artificial bicarbonate buffered brine, with the only major change in the experiments overall, being an increase in alkalinity of the waters. The reactions targeted to occur during the experiments included anorthite to calcite and kaolinite, albite to smectite and quartz, and annite to siderite, muscovite and quartz; however, given that the system was strongly buffered with bicarbonate, the pH was never acidic enough for these reactions to occur. The experimental conditions were more suited to far-field mineral-trapping precipitation than dissolution, but for this to have occurred then cations such as calcium and iron would need to have been present in the solution.

Krumhansl et al. (2003) used natural sodium chloride dominated formation waters for their batch reactions with sandstone at 40°C and 48 bars, and concluded that carbonate cement dissolved, and plagioclase corroded whilst K-feldspar did not, and kaolinite precipitation occurred over a 19-month period. It is possible, though, that K-feldspar simply wasn't present in significant abundance within the actual samples tested, as its abundance in the parent sample was about 5% in comparison to 26% albite. Under the stated experimental conditions of 48 atm partial pressure of CO₂ at 40 degrees Celsius, the system pH should have been 4.5 or less, which is well below the pH threshold at which the geochemical modelling performed by the authors predicted that K-feldspar should have reacted (pH = 5.6). Given that one would expect all kinds of feldspar to have roughly similar reaction kinetics, if plagioclase feldspar reacted appreciably, then K-feldspar should have too (e.g. Labus and Bujok, 2011). Whilst a natural formation water was used in an effort to limit disequilibria reactions due to imbalance between samples and the ionic composition of the water used in the experiment, a natural formation brine is difficult to sample and store without change. Conversely, it is also very difficult to make artificial brine in the laboratory due to most components generally having lower solubility at ambient conditions. Thus, regardless of what kind of water is used during experiments, it is essential for the study authors to demonstrate how they have distinguished between changes in water chemistry due to just sample

exposure to the water (or even without a sample, just pressurizing and heating the water beyond the conditions at which it was created), as opposed to reactions of minerals with carbonic acid.

Rosenbauer et al. (2005) used both natural and artificial formation waters in their batch reactions with sandstone and limestone samples at temperatures and pressures of up to 120°C and 600 bars, taking small samples periodically for analysis, and found that concentrations of dissolved ions changed non-linearly over time. Porosity increases were possibly offset by precipitation of anhydrite and other salts during CO₂ desiccation of samples. The use of flexible titanium-lined gold reaction vessels greatly reduced the potential for the reactor to corrode and metal ion release to contribute to reaction water chemistry. Both cations and anions were assayed, and the XRD analysis of the solid powder samples used was performed before and after experiments. Kaszuba et al. (2003) and Kaszuba et al. (2005) similarly used Ti-lined gold reaction cells, and found that silicate minerals were etched and magnesite precipitated during their ~ 1.5 month-long experiments using artificial brine at 200°C and 200 bars. Artificial brine was allowed to equilibrate with samples prior to addition of CO₂ to the system. Brine chemistry both before and after CO₂ injection changed non-linearly with time, and some changes such as a decrease in chloride concentration were unexplained. It could be that the ion chromatography method used to analyse anions was affected by the presence of certain cations in the solutions tested.

Bertier et al. (2006) found alteration of alumina-silicates and dissolution of carbonates occurred during their eight month long experiments with sandstone samples at 80°C and 150 bars, and suggested that precipitation of minerals upon the batch reactor internal surface may also have occurred. However, it is difficult to know if the material observed on the walls of the batch reactor was in fact precipitation that occurred during the experiments under high pressure, occurred during de-pressurization of the apparatus, or was partially or totally very fine detrital material washed out of the samples.

Wigand et al. (2008) concluded that montmorillonite precipitation occurred in response to albite dissolution by experimentally produced carbonic acid, on the basis of SEM images post-experiments showing altered albite crystals surrounded by montmorillonite. Minerals such as K-feldspar and dolomite also reacted whereas illite, kaolinite and quartz appeared to be unaffected after 1500 hours exposed to carbonic acid at 60°C and 300 bars. Although albite does alter to smectite, it is possible that at least some of the montmorillonite observed was present surrounding albite grains prior to the experiments, having formed due to natural exposure of the samples to a CO₂-containing fluid or else due to past near-surface weathering.

In contrast, rather than precipitating, Lima et al. (2011) found evidence of the smectite within I/S layers having partially dissolved along with feldspars, with TEM suggesting crystallisation of new illite within the I/S structures in samples exposed to carbonic acid at 80°C for 6 months and up to 12 MPa pressure. Whilst these experiments were up to four months longer in duration, used artificial NaCl brine ten times more concentrated than that of Wigand et al. (2008), and were performed at lower pressure, the major difference was the higher temperature. This combined with lower pressure means that the pH of the system of Lima et al. (2011) was less acidic than that of Wigand et al. (2008), and yet smectite was indicated as having dissolved during the experiments of Lima et al. (2011) rather than precipitated. The higher temperature of the experiments was possibly the reason for new illite nucleation.

Ketzer et al. (2009) found precipitation of opal as well as carbonates after 100 hour long experiments with sandstone samples at 200°C and 100 to 150 bars. This was partially in response to dissolution of reactive silicate minerals such as feldspars. Some of the crystal forms observed in the precipitated phases were quite unusual, and potentially some could be artifacts of the vacuum filtration method used to separate solids from the reaction fluids, or else may have formed within the wet supercritical CO₂ upper portion of the reaction vessel.

Heeschen et al. (2011) observed iron mineral precipitation over the surface of dolomite crystals after samples had been exposed to carbonic acid for 160 hours at 120°C and 200 bars; this may have prevented the dolomite from completely dissolving.

Similarly, Liu and Maroto-Valer (2010) found that iron hydroxide precipitated along with calcite during un-buffered CO₂-sandstone-brine experiments over a range of temperature and pressure conditions, with strontianite precipitating as well during buffered experiments.

Labus and Bujok (2011) found that potassium feldspars were more etched than sodic feldspars after 75 days carbonic acid exposure, and that clays and dawsonite were precipitating. This was in contrast to earlier studies (cf. Krumhansl et al., 2003), which found that sodic plagioclase was etched whereas potassic feldspar was not after 19 months exposure to carbonic acid. But as previously discussed, it is possible that earlier studies didn't observe significant K-feldspar within reacted samples. The observation that dawsonite precipitated is interesting given that many experimental studies have not reported dawsonite formation in spite of many predictions of dawsonite formation reported by geochemical modelling studies (cf. Hellevang et al., 2011). As discussed by Hellevang et al. (2011) and demonstrated experimentally by Bénézech et al. (2007), dawsonite is only likely to form at pH's more alkaline than 9, is unstable at pH less than 9 and dissolves below pH 6.5. Other processes such as nucleation, buffering by silica-bearing minerals, and multiphase reaction kinetics can severely limit the conditions under which dawsonite will actually form. The modelling software predictions of wide-spread dawsonite formation were likely due to only thermodynamic parameters being considered as reaction limiting, rather than other considerations such as nucleation conditions and reaction kinetics (cf. Hellevang et al., 2011).

2.1.2. Continuous flow-through studies

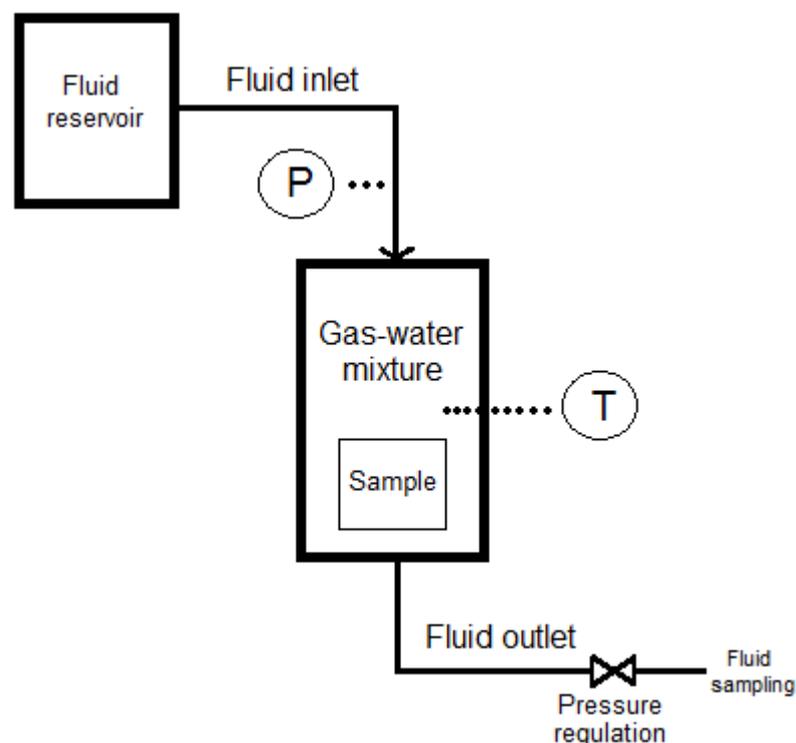


Figure 2: Generic sketch of a continuous flow geochemical reactor

Some studies such as Shiraki and Dunn (2000) periodically measured the chemistry of core-flood waters and found partial dissolution of minerals such as feldspar and anhydrite, confirmed by SEM observations,

which also showed that some new kaolinite had precipitated. Porosity change was variable, with up to a 44% increase in some cores, whereas other cores did not exhibit any permeability change and even showed decreases in porosity. One of the difficulties with this type of experiment is the fact that the pathways preferentially taken by fluids flowing through rocks may not involve contact with many, if any, reactive minerals due to these being shielded from the fluid by less reactive minerals. This could be the reason for the variable porosity change observed, rather than there simply not being reactive minerals present.

Shi et al. (2011) investigated sandstone porosity using X-ray CT and Hg-porosimetry. Porosity heterogeneity was found to have a large impact upon fluid flow pathways of CO₂ through the core samples.

Bacci et al. (2011) found that fluid flow “worm holes” formed through their limestone samples in response to core flooding with carbonic acid, and thus porosity and permeability had increased as a result of this.

Scislewski and Zuddas (2010) used SEM to show that mineral alteration products had grown over the surface of primary grains during continuous flow reactor experiments with mafic rocks over 50 days under surface temperature and pressure conditions, and inferred that such coatings were a great influence upon overall mineral dissolution rates. Similarly to the problem of potentially reactive fluids not being able to contact reactive minerals due to shielding by less reactive minerals, alteration surfaces formed upon individual mineral grains during experiments can act to slow reactions, or even terminate them (similar to aluminium reaction with oxygen in the air).

2.1.3. Summary and analysis

The majority of laboratory geochemical studies have used batch reactor-type set-ups rather than continuous-flow reactors as this simplifies the experimental procedure and results in higher concentrations of dissolved components in the reaction fluids, simulating near well bore environments. Batch reactor-type experiments have been conducted with powders, chips and cores under a range of temperature and pressure conditions representing the near surface to several kilometres depth for periods from a few days to 19 months. Sample mineralogy has been similarly variable with a focus on mineralogically complex sandstones that have the most potential to exhibit dissolution and precipitation reactions when exposed to carbonic acid. Outcomes with respect to observed mineralogy changes have been mixed, mainly corresponding to the complexity of the system being probed. General observations are that calcite and dolomite cements are dissolved, and feldspar minerals are variably etched with precipitation of ferroan carbonates and clays observed in many of the longer term experiments. In some cases, however, it is not clear whether the precipitates formed under ambient conditions in the reactor or during depressurization of the system. A related problem is one of analysis of the system under realistic conditions. While the experiment may be conducted under high pressure and temperature conditions, sample chemical analysis is virtually always done at ambient pressure, which changes the outcomes.

The main gap to be addressed in this project is the lack of integrated studies assessing *both* the geochemical and physical changes to the same target rocks and fluids during CO₂ sequestration in sandstone, both experimentally in the short term, and longer term by modelling. Geochemical and physical effects from CO₂ storage are site specific, i.e. site specific mineralogy and rock structure will affect the dissolution and precipitation reactions which ensue. Hence, targeted rock specific experiments are needed. An outline and discussion of suggested experimental procedures is as follows:

a) Sample characterization and evaluation methods (both solid and fluid):

To assess rock sample property changes caused by reactions with carbonic acid, it is imperative that samples be well characterised both before and after the experiments. Specifically, sample-specific properties such as dry mass and helium pycnometry to help determine sample density changes, SEM-EDS and/or QEMSCAN analysis of sample surfaces, X-ray micro-CT scanning, and photographic records of sample appearance before and after experiments would be useful. Other characterisation analysis, using sister-sample off-cuts, could include XRD, optical microscopy, permeability, and mercury porosimetry, with such analysis also potentially being done on actual samples post-experiment. At the very least, knowing the mass of each sample tested, and the volume of water in each experiment and fluid test sample, will assist in normalising results to make true comparison between different sample experiments possible.

The water composition chosen for experiments depends upon exactly what variables are to be tested in a given experiment. Irrespective of which kind of fluid is used, there must be a clear understanding of starting fluid composition prior to interactions with rock samples. Therefore, the same analysis of fluid composition must be done before, after, and potentially during experiments. ICP-OES (aka ICP-AES) can accurately determine major, minor, and some trace element concentrations for most dissolved chemical species of interest, but not anions (other than total sulfur and phosphorous present in solution). Immediately after sampling from the experimental apparatus, the fluid samples should either be refrigerated or else must be acidified to pH <1 to limit precipitation of carbonates and other species stable at atmospheric conditions. Filtering should not be required if solid samples are used, or powdered samples are contained within dialysis tubing. Ion chromatography of non-acidified samples can measure anions such as chloride, but not bicarbonate as this is generally removed by instruments prior to analysis of fluids for anions. If the gas phases present are also of interest, the experiment system could be hooked up to high-pressure gas chromatography (HPGC) or even supercritical fluid chromatography (SFC) analysis apparatus.

b) Experimental and analytical blanks:

To make fluid analyses as comparable as possible, and limit sources of error, different kinds of “blank” tests should also be done. These include measuring the starting composition of each fluid used for each sample experiment (in case this varies, even if not meant to), internal blanks during ICP-OES (the stock nitric acid fluid used to make the standards etc.), experimental system blanks (e.g. pressurized water-nitrogen experiments done in a clean system under the same conditions as rock sample experiments), and analysis of sample-water interaction (without carbonic acid present, and preferably at test pressure). The experimental system blank experiments are probably the most critical, as these largely determine the background concentration of elements either present in the lines post-cleaning between experiments, or else leached out of the system materials during experiments. Ideally, experimental system blanks should be done between all experiments, but instrument time constraints may mean that it is not feasible to do this each time for the length of time under which samples are tested. At the very least, after cleaning the apparatus, a system blank experiment of a couple of days duration should be done and the water analysed to get an idea of the potentially changing background concentration of residual sample-derived material left within the system from the previous experiment.

c) Some key constraints imposed by the chosen experimental and analytical method(s):

If incremental fluid samples are to be taken during batch reactor experiments, sufficient fluid volume must be present initially in order to keep samples immersed for the duration of the experiment, and to

not have loss of volume causing supersaturation of dissolved species towards the end of the experiment (if those species wouldn't have been at saturation levels in the initial volume of fluid). Continuous flow apparatus should either have sufficient initial fluid volume to maintain the experiment at the chosen flow rate, or else a way of adding additional fluid to the system without adversely affecting the sample and experimental conditions. Whether samples are taken incrementally from a batch or continuous flow reactor, all fluid samples for a given sample should be analysed via ICP-OES at the same time using the same standards in order to achieve greatest inter-comparability of samples relating to a single experiment. Although the analytical errors associated with using different standard solutions for different analysis runs are small, such differences are always present. If inter-sample variations of ions of very low concentration are of interest, then it is recommended that the measured intensity data (corrected) for each ICP-OES analysis run is reprocessed off-line (in an Excel spreadsheet) using intensity/concentration data from a single set of calibration standards in order to minimise differences in apparent concentrations determined resulting from changes in the slope of calibration lines for different days of analyses. Otherwise, ICP-MS may be used to determine trace element concentrations if required, but this is not really applicable for concurrent major element analysis as concentrated fluids cause MS detector damage or else lower the analytical accuracy of the instrument, and dilution may eliminate the possibility of trace element detection.

2.2. Laboratory geomechanical studies

When subsurface conditions are changed, including as a result of CO₂ injection for sequestration, the rock mechanical properties, fluid thermophysical properties, and the system properties including anisotropic/3D flow network properties, evolve in time. These properties influence the quantity and rate that CO₂ can be injected, the ways that it flows, migrates, and where and how it is ultimately trapped.

An aim of this project is to determine the anisotropic and dynamic properties of sandstone reservoirs relevant for CO₂ geosequestration, and through location-specific case studies, confirm the extent of the economic impact of better directional and dynamic permeability evaluation.

It is well known that any change to reservoir equilibrium state of stress through withdrawal or injection may result in compaction and surface subsidence, or the reverse, and/or formation damage. This is a critical factor with respect to the design of the casing platforms and to the overall reservoir performance.

To better address the issues concerning CO₂ geomechanical effects in a reservoir, this second aspect of the project will broadly analyse the approaches that have been made by preceding researchers in order to develop an optimised method and technology for CO₂ sequestration. *Mainly it will explore the basic geomechanic properties, permeability/porosity alteration, and experimental studies.*

As with geochemistry, many of these properties are very much location specific, and finding ways to understand and untangle the physics in a way that makes modelling and prediction tractable and elucidates the effects of carbonic acid upon porosity, permeability, and rock strength has been the subject of a substantial body of research.

2.2.1. CO₂ intraformational transport studies

An important issue to be addressed is understanding the way that injected CO₂ displaces water in the storage volume. Petrophysical character, gravitational effects, gas phase behaviour, and mass transfer by molecular diffusion and dispersion processes are among other factors that determine the amount of CO₂ that can be injected.

The resistance to fluid flow in a porous medium determines injectivity. The relative permeability of a phase will be a function of the fraction of pore spaces contributing to its cross-sectional flow. This means that the overall effective permeability of a medium that contains two fluids will be lower than its absolute permeability (Richards, 1931).

The preference of a porous material to be covered (or wet) by one of the phases, and the interaction between the fluid phases and the pore wall involves capillary forces and ultimately influences the fluid distribution in the medium. The wetting phase (brine saturated with CO₂) tends to distribute over a high capillary region (the small pores) thus minimizing the contact angle with the pore wall. By contrast, the nonwetting phase (CO₂ fluid saturated with water, and assuming the formation was not dry to start with) has a preference to occupy the space in the middle of the larger pores to maximize the contact angle with the wall. The difference in fluid distribution causes the dissimilarity in relative permeability of the wetting and the nonwetting phase.

Relative permeability plays a major role in determining ultimate recovery and therefore also ultimate storage in a reservoir (Jerauld, 1997). Obtaining relative permeability for CO₂-brine systems is of great importance to help design, optimize, and analyse the displacement process.

Lee et al. (2010) performed multiple core-flooding experiments upon a single core of Berea sandstone in order to calculate relative permeability of different CO₂-brine mixtures, with Darcy flow assumed. Endpoint relative permeability of CO₂ was found to increase with decreasing viscosity ratio (Lee et al., 2010).

The fraction of CO₂ that will be entrapped in a reservoir by capillary forces and solubility is very important for predicting the sequestration volume. Land (1968) developed a model to predict trapped gas saturation as a function of the initial gas saturation in water-wet sandstone cores. Land's model which is the most used empirical trapping model, and most relative permeability models, have been assimilated with hysteresis functions by Killough (1976) and Larsen and Skauge (1998).

At a given saturation, CO₂ plume migration in porous media could be the function of several macroscopic transport properties such as relative permeability, capillary pressure and dispersivity. As experimentally determined, these properties depend on fluid saturation, saturation history, fluid properties (viscosity, density and composition) and pore space morphology. Furthermore, disconnected droplets can build up significant resistance to flow and cannot be dragged along by the continuous flowing of a phase because of Jamin's effect (Calhoun, 1953).

For wet mixed rock types Jerauld (1997) initiated a new model that is dependent on the observation of initial residual curves of the non-wetting phase in a mixed wet medium.

Another important factor that affects the displacement front of CO₂-brine is interfacial tension (IFT) (cf. Bennion and Bachu, 2006). Interfacial tension may be seen as the amount of energy required to create a unit area of interface (Gennes et al., 2004; White, 1972) or as the force per unit length acting along an arbitrary line on the interface. If lower IFT occurs near the injection well a piston-like displacement will be achieved. For example, many experimental studies that have been carried out at low interfacial tension indicated relative permeability of the fluids was enhanced if compared to the relative permeability of two phases measured at high interfacial tension (Bardon and Longeron, 1980; Haniff and Ali, 1990; Jerauld, 1997; Schechter and Haynes, 1992).

When the interfacial tension between two phases becomes sufficiently low, the capillary forces that formed would be weak and can be neglected with regard to the viscous forces caused by friction within the flowing fluids. As a result, the ratio of the viscous forces to the capillary forces induces a change in flow regime and thus relative permeability curves approach the trends of ideal phase's curves. In summary, fluid phase permeability is specific to a given porous medium, and is correlated with features such as pore geometry, porosity, tortuosity, and specific surface area (Carman, 1937; Kozeny, 1927).

2.2.2. Geomechanical effects of CO₂ sequestration

The stress-strain relationship of a reservoir has been extensively investigated by numerous researchers and it is influenced by a large number of factors, such as the lithology, degree of cementation and cementing material, fluid saturation, compressibility of the rock matrix and fluids, porosity and permeability, and reservoir pressure and temperature (e.g. Arsyad et al., 2011; Egermann et al., 2006; Ferronato et al., 2010; Oikawa et al., 2008; Rimmelé et al., 2010; Ross et al., 1982; Shukla et al., 2012; Zemke et al., 2010).

Colback and Wild (1965) concluded that the compressive strength of shale and quartzose sandstone under saturated conditions were approximately half what they were under dry conditions.

Fatt (1958)'s results showed there is no practical correlation between the compressibility and porosity. This is contrary to the observation made by Hall (1953), who stated that with decreasing reservoir pore pressure the compressibility of any reservoir rock will be controlled by two factors: poro-elastic expansion of the individual rock grains and the additional formation compaction brought about as a result of pore pressure depletion. At field scale only the vertical component of hydrostatic stress is constant while horizontal stress components are controlled by the formation boundaries (Geertsma, 1953).

The change in pore pressure is not the only variable governing the CO₂-geomechanical equation, as the matrix, bulk and pore compressibility are expected to change with time due to fluid interactions. The pore compressibility of sandstone acquired from triaxial strain tests is nearly twice the magnitude of the C_p obtained from uniaxial tests (Sfer et al., 2002). The degree of the pore-pressure change, ΔP_p , in the reservoir for a given change in pore volume depends on the compressibility of the pore fluid; C_{fi} .

Carbon dioxide undergoes a large change in density near the critical pressure and temperature. Despite the conclusion made by Ren (1979) that 'the effect of fluid compressibility is more pronounced if the rock is saturated with an incompressible liquid than with a compressible gas', the severity of CO₂ interaction with its surrounding host rock in such conditions may have an imminent consequence on the rock strength.

Reactive-transport experiments in the presence of CO₂ have been performed in sandstones (e.g. Rimmelé et al., 2010; Ross et al., 1982; Zemke et al., 2010) and carbonates (e.g. Grigg and Svec, 2003; Rimmelé et al., 2010; Svec and Grigg, 2001). Results have indicated that a modification of the rock structure can either improve or impair the matrix permeability. Rimmelé et al. (2010) did month long autoclave type experiments with cores of sandstone and limestone in carbonic acid and distilled water, and found that mechanical properties were unaffected, with there being only a slight increase in sample permeability, but decreased weight and density with increased porosity, and yet observed no significant changes in pore size distribution and sample mineralogy.

The sample characterisation and analysis procedures were comprehensive, but it is possible that the need to use sister samples for certain tests such as pore size distribution via Hg-porosimetry made it difficult to detect any changes in these parameters, and that the month-long timeframe of the experiments was insufficient to significantly change sample mineralogy.

Zemke et al. (2010) used NMR as well as Hg-porosimetry to monitor porosity changes in sandstone samples exposed to carbonic acid for either 6 or 15 months, and found a slight increase in porosity corresponding to a shift in pore size distribution towards larger pores.

The permeability of rock samples saturated with CO₂ increases with increasing stress as the rock sample approaches failure under compression (Shukla et al., 2012). In the post failure stage, the permeability dramatically decreases with the increasing confining pressure that closes the fractures and may rearrange the rock constituents (Shukla et al., 2012).

Nevertheless, permeability increases are rather limited even in the case of very pronounced porosity increases (4-5 times) (Egermann et al., 2006).

Arsyad et al. (2011) have studied low permeability rock samples and observed that the injection of supercritical CO₂ generates an increase in the pore pressure leading to an elastoplastic deformation. As a consequence, the permeability and porosity of the sandstone increased by 2.6% - 3%. There was no fracture caused by injection, even when the hydraulic pressure exceeded the confining pressure.

Low permeability rock has been found to be undamaged and with full integrity under CO₂ injection even when the injection pressure is close to the lithostatic stress (Ferronato et al., 2010).

Egermann et al (2006) stated that rock weakening following CO₂ injection is more pronounced for the shear modulus than the drained bulk modulus, which displays a significant alteration of the cementation as compressive stress is reduced. On the other hand, Oikawa et al. (2008) showed the differences in strength between the water-saturated and the CO₂-injected test pieces were very small under the same simulated *in situ* conditions.

Well treatments such as acid stimulation have long been employed by well engineers, particularly in carbonate rocks, to increase relative injectivity at the near well bore region; the increments depend on injection rate/flux, cumulative injection and strength of the stimulating acid (McDuff et al, 2010).

The stages of rock deformation have been experimentally studied using an acoustic emission (AE) technique. As a rock sample underwent compression or tension, stress produced rapid releases of energy. The energy release is in the form of very low level seismic events or elastic waves of sound which can be traced by (AE) sensors. This non-destructive method of rock study has been used by several researchers to predict and analyse a rock's strength relative to the induced stresses (cf. Eberhardt et al., 1999; Tang and Kaiser, 1998). The same technique has been used to investigate several stages of rock failure such as crack closure, crack initiation, elastic crack damage and final macro-level rock fracturing (Cai et al., 2007; Ranjith et al., 2008; Shukla et al., 2012). Egermann et al. (2006) used a CT scanner and NMR T2 to measure porosity profile and developed a methodology to alter rock samples in a controlled and homogeneous manner in order to investigate the evolution of the petrophysical, mechanical and petro-acoustical properties.

Ojala (2011) measured the tensile strength of various reservoir and cap rock analogues. The effect of CO₂ on tensile strength was investigated by exposing rock discs to CO₂ saturated salt water. The CO₂ tested samples were sister samples of others that had been aged in salt water. However, the tensile strength did not appear to be affected by the CO₂ environment. Their experiments suggest that the tensile strength is a function of rock porosity and p-wave velocity.

2.2.3. Summary and analysis

Investigating the shear strength of the reservoir rock near the injected wells is important for CO₂ geosquestration projects because the formations will vary in strength. As the displacement front moves away from the wellbore the stress profile will change radially depending upon the magnitude of build up pressure, permeability, and fluid properties. Nonetheless, the relationship between the strength and elastic properties for a given rock measured at laboratory and reservoir condition near the wellbore is still not well understood, and in this project a practical step will be to strive to better explain the relationship between 3D stresses and rock strength following CO₂ injection using our true triaxial stress/strain rig. Each storage site will have its own site-specific attributes which result in different ranking of the impact of these attributes between sites.

The ability of the rock samples to resist stress without yielding or fracturing under the potential reservoir conditions of our study will be evaluated. Although rock strength is affected by the mineralogy of the

rock and by the character of the grain contacts, the main factor will be whether, and how, carbonic acid-rock reactions adversely affect sample stability post CO₂ injections.

This research also investigates the effective pore volume that would be available for CO₂ geosequestration giving the consideration of geomechanical and geochemical properties of the targeted zones. Moreover, it will strive to develop a practical model to predict the flowing fraction of CO₂ that will be entrapped in a reservoir by capillary forces, solubility and heterogeneity.

The factors that affect fluid flow and distribution in reservoir porous media will be investigated collectively and thoroughly using dynamic reservoir simulation that incorporates the influence of relative permeability, IFT, and wettability as well as stress-strain relationship post CO₂ injection.

2.3. Image analysis and X-ray CT for pore-network and mineral distribution modelling

Peters et al. (2006) used synchrotron X-ray micro-CT scanning of sandstone to map 3D pore-structure and quantify internal surface area. SEM-BSE images and SEM-EDS mapping was also undertaken for thin-section slices of the sandstone during the studies of both Peters et al. (2006) and Peters et al. (2009), with a MATLAB image processing tool used to determine 2D porosity and distribution of different grain compositions. With the exception of quartz these were not specified in Peters et al. (2006), whereas many different minerals were identified by Peters et al. (2009). The combined X-ray CT and SEM porosity and grain distribution data were used to create a 3D pore network model, with the intention of eventually up-scaling the model to improve simulation of geochemical processes during geosequestration of CO₂.

Golab et al. (2010) and Knackstedt et al. (2012) combined X-ray micro-CT scanning of 8 mm (or less) diameter sandstone and siltstone cores with QEMSCAN analysis of sections cut from the cores to image and assess primary and secondary porosity. QEMSCAN is a more holistic and larger-scale technique than SEM-EDS mapping, which can only examine small areas (millimetres or less) and analyse a few different elements at a time. The combined X-ray CT and QEMSCAN data were integrated to develop 3D pore-network visualisation. Golab et al. (2012) recently undertook similar work with coal cores, and were able to establish the distribution of different mineral phases occluding natural fractures within the samples. Incorporating similar 3D porosity network images of our samples with our multiphase-flow models will help to make them more realistic. It may also be possible to combine the QEMSCAN mineral ID data with X-ray density maps of the section from which the QEMSCAN sections were cut, to create a 3D mineral phase distribution map.

3. Modelling

3.1. Geochemical modelling

Numerous geosequestration modelling studies have been undertaken (Tables 2a,b,c), including modelling-only studies (e.g. Ennis-King and Paterson, 2007; Knauss et al., 2005; Peters et al., 2006; Pham et al., 2011; Xu, 2008; Xu et al., 2004a; Xu et al., 2004b; Zwingmann et al., 2005), and coupled experimental-modelling studies (e.g. Gunter et al., 1997; Heeschen et al., 2011; Ketzer et al., 2009; Kirste et al., 2004; Krumhansl et al., 2003; Labus and Bujok, 2011; Massarotto et al., 2010; Scislewski and Zuddas, 2010; Soong et al., 2004; Wigand et al., 2008; Xu et al., 2005) to assist us to understand the water-rock-CO₂ interactions and to predict the changes that may occur in the host formation. In this ANLEC R&D project, the modelling work is concerned with the temporal and spatial distribution of formation permeability, particularly in the near-well area, as a result of the energised fluid flow and water-rock-CO₂ interactions. Increased permeability over time within the storage reservoir could suggest that less injection wells are needed. However, increased permeability over time in the caprock layer could suggest risks. Therefore, an accurate prediction on permeability change is critical. For our present

efforts to be an improvement in modelling science and techniques, it is important to know what has been done before.

3.1.1. Legacy models

Gunter et al. (1997) used PATHAR.94 to model dissolution and precipitation reactions that may take place on the basis of an initial mineralogy derived from sample analysis, an initial artificial bicarbonate brine chemistry, and an arbitrary mineral reactive surface area, and found that on average it took 50 years for appreciable reactions to take place in their system. However, the corresponding batch reactor experiments showed no change in mineralogy and only an increase in alkalinity due to the buffering of the system causing the pH to not be acidic enough for reactions to occur during the timeframe of the experiments. PATHAR.94 has since been replaced by a model called GAMSPATH, which is continuously upgraded.

The Fortran program EQ3/6 has been used to model dissolution and precipitation reactions in geosequestration systems (cf. Zwingmann et al., 2005), but is not user-friendly in that it produces large quantities of text output, requiring further data mining. Krumhansl et al. (2003) did reaction path modelling using both EQ3/6 and REACT, and found that simply in-putting brine compositions into a geochemical program resulted in the projected presence of minerals that do not exist within rock samples characterised for the source formation of the brine. Therefore, a list of suppressed phases must be created based on geochemistry knowledge and experience. By comparing the data base in EQ3/6 and REACT, Krumhansl et al. (2003) also raised the critical issue in geochemistry modelling, i.e. the data base integrity and correctness, and the correction of analyses.

3.1.2. PHREEQC and GWB

Kirste et al. (2004) used PHREEQC to model ion speciation, mineral saturation, and pH and GWB to model kinetics and equilibrium based reaction paths for a sample based upon the composition of a sequestration target formation. Kirste et al. (2004) found that variation of mineral reactive surface area results in orders of magnitude differences in overall mineral reaction timeframes for the system. The high sensitivity to the reactive surface area raised an important question that is how to determine the reaction surface area accurately?

PHREEQC has been used to model dissolution and precipitation kinetic reaction pathways for a number of mineral and formation water compositions relevant to a geosequestration target (e.g. Heeschen et al., 2011; Ketzler et al., 2009; Pham et al., 2011; Scislewski and Zuddas, 2010; Wigand et al., 2008; Xu et al., 2004a). Ketzler et al. (2009) concluded on the basis of modelling of their experimental system that carbonates formed were not due to carbonation of the brine used, but rather were likely depressurisation re-precipitation of carbonates dissolved during the experiments as the modelled pH was too acidic for brine carbonation to have occurred. As discussed by Krumhansl et al. (2003), it is essential that the databases used by models include CO₂-system applicable data so that predictions generated are realistic, and thus able to be used to scrutinise experimental results (and vice-versa) as Ketzler et al. (2009) did.

Scislewski and Zuddas (2010) proposed that overall mineral reaction rates depend upon the stability of early-formed alteration mineral coatings of primary mineral grains observed during their experiments, which are not taken into account by conventional models.

Kampman et al. (2009) investigated a natural CO₂ accumulation and modelled mineral reaction rates based upon the distribution of formation water compositions and corresponding drill-core sample mineralogy. Their assumption that groundwater flow was homogeneous across the field may explain the difficulty in interpretation of carbonic acid effects upon the field.

Ketzer et al. (2009) did experiments as well as limited kinetic modelling of reaction water chemistry using PHREEQC, which suggested that only limited reactions would have occurred for most minerals aside from calcite, as expected.

Pham et al. (2011) questioned the formation of dawsonite predicted to occur in their PHREEQ model as it isn't necessarily observed in fields that have experienced natural CO₂ flooding events, and highlighted a need for more experimental data on clay dissolution rates and mineral nucleation and precipitation rates in general.

An issue with the PHREEQC program is that it uses Pitzer-type equations to describe chemical behaviour and the parameters of its database are only valid for reactions at 25°C. The Debye-Huckel type activity model supported by PHREEQC is able to calculate parameters up to 150°C, but can only explain departures from ideality for very dilute and perfectly ionic solutions of spherical dissolved species. Furthermore, there may not be any reliable data relevant to certain species commonly encountered in a geosequestration system, such as dissolved silica in carbonic acid. The expressions used by PHREEQC to account for non-ideality of brine ion-interaction are not sufficient to describe high ionic strength solutions (Soong et al., 2004), which can be encountered especially in offshore geosequestration targets. Soong et al. (2004) used PHREEQC to model brine carbonation potential under the assumption that the ideal gas law is applicable to CO₂ behaviour in geological systems (which it isn't generally). Programs like PHREEQC and GWB cannot take account of multiphase fluid behaviour. However, GWB does include kinetic and thermodynamic data that can be used for temperatures other than 25°C for many species, and so is more applicable than PHREEQC to describing geological conditions. We intend to use GWB for part of the modelling aspect of our current ANLEC project.

Regardless of which modelling program is used, the stock database parameters available in the off-the-shelf product will need adjusting. Values for some species may be missing or not cover the temperature range to be explored. Krupka et al. (2010) undertook a comprehensive literature review of available thermodynamic data for geochemical modelling. However, non-carbonate mineral reaction rates may be 3 to 8 orders of magnitude less than carbonate-carbonic acid reaction rates (Sorensen et al., 2009; Svensson and Dreybrodt, 1992; Xu and Pruess, 2004), and this is often not taken into account within databases used by modelling software. Rates of mineral dissolution reactions differ depending upon which acid is used, and the surface area of the minerals reacted, in addition to other parameters such as temperature, pressure, and the starting ionic composition and strength of the solutions analysed.

3.1.3. TOUGHREACT

Other programs such as TOUGHREACT can take account of multiphase fluid behaviour and thus better describe CO₂ in the subsurface. TOUGHREACT is able to model both mineral dissolution and precipitation, and has been used in reservoir modelling for single well studies.

TOUGHREACT has been used to take account of parameters such as chemical and physical heterogeneity of fractured porous media, fluid flow relative to pressure and gravity, capillary pressure, diffusive and conductive heat flow, advection and molecular diffusion, hydrodynamic dispersion, evolving porosity and permeability, and mineral reactive surface area (Ennis-King and Paterson, 2007; Xu, 2008; Xu et al., 2004a, 2005; Xu et al., 2004b). The reaction-induced changes in mineral surface areas has a dramatic effect upon reaction times (Xu et al., 2004a).

The program TOUGHREACT is sufficient to predict the logical greater capacity of mafic minerals to react with and sequester CO₂ in comparison with felsic minerals (cf. Xu et al., 2004a), plus it couples geochemical reactions with convective mixing and other physical mass transfer mechanisms. TOUGHREACT is also a fast evolving software with continuous improvements on model correctness. (Xu et al., 2011).

3.1.4. CRUNCH

Knauss et al. (2005) used CRUNCH to model co-contaminant CO₂ geo-sequestration. Parameters included diffusive, dispersive and advective transport, multicomponent aqueous complexation, unsaturated transport with aqueous-gas phase exchange, kinetically-controlled mineral precipitation and dissolution (EQ3/6 database), multicomponent ion exchange on multiple sites, multicomponent surface complexation on multiple sites with/without electrostatic correction, microbially-mediated reactions, radioactive decay chains, advective transport of solid phases, and multicomponent diffusion with electrochemical correction for differences in diffusion coefficients. It was possible to use fixed activity, total concentration, equilibration with mineral or gas phase as initial boundary conditions.

CRUNCH is also capable of modelling non-isothermal reaction and transport; however, isothermal, isobaric fully saturated conditions were assumed for the study of Knauss et al. (2005). Spherical grains were assumed for the purposes of determining mineral reactive surface area, iron was assumed to be in equilibrium with pyrite, and SO₂ was assumed to be eventually oxidised to sulfate. TOUGH2 was used to model CO₂-only transport. But as for TOUGHREACT, although TOUGH2 is capable of dealing with multiphase behaviour, it is a relatively simplified fluid flow model as it assumes Darcy flow, and so cannot deal with complexities that arise with real fluid flow behaviour that is non-Darcy (Knauss et al., 2005; Xu et al., 2004a). SO₂ was found to have a significant impact upon the reactions that took place, due to the dramatic lowering of pH, whereas co-injection of H₂S and CO₂ was little different to a CO₂-only system (Knauss et al., 2005), even for significant amounts of H₂S as shown also by (Xu et al., 2004b).

3.2. Reservoir modelling for geosequestration

As the practical importance of simulating complex nonlinear processes in heterogeneous porous media systems becomes increasingly apparent (e.g. for hydrocarbon recovery, CO₂ geosequestration and others), a number of computational modeling methodologies have been developed to address such behaviors. In the past few decades, numerous numerical simulations have been conducted and compared with experimental results or field observation (Bear and Bachmat, 1990; Buldyrev et al., 1992; Kaviany, 1995; Nield and Bejan, 2006).

A number of CO₂ geosequestration reservoir-scale modelling projects have been done (e.g. Arsyad et al., 2011; Eshiet and Sheng, 2011; Flett et al., 2005; Juanes et al., 2006; Lee et al., 2009; Nicot, 2008; Person et al., 2010; Qi et al., 2009; Shi et al., 2011).

Qi et al. (2009) modelled dispersion and dissolution of CO₂ in water, relative permeability, and capillary trapping, for brine-CO₂ co-injection followed by brine-only injection. The simulation was based upon the 3D model for a heterogeneous North Sea aquifer (SPE10 reservoir model, Christie, et al., 2001), and like many reservoir models did not include consideration of geochemical reactions.

Nicot (2008) developed a regional aquifer flow model using the programs MODFLOW96 and PMWIN to simulate water-table response to field-scale CO₂ injection over the life of a hypothetical geosequestration project. The model incorporated aquifers and aquitards, formation thickness ranges, horizontal and vertical permeability, porosity and storativity, outcrop and geopressurized zone boundaries, and CO₂-water behaviour over a 100 year timeframe. CO₂ was assumed to remain supercritical, not dissolve into groundwater, not react geochemically with the formation or dissolved ions in groundwater, and be unaffected by variations in salinity. The injection pressure of 75% lithostatic was assumed to be insufficient to cause fracturing, and the model boundaries were assumed to experience zero fluid flow. The model projected a negligible water table rise of approximately one metre over 50 years.

Person et al. (2010) developed a sharp-interface model that utilised end-point relative permeability and phase saturation to model field-scale CO₂ injection and multiphase behaviour within a hypothetical

reservoir. Measured porosity/depth and permeability/depth relationships were incorporated into the model. Pore pressure and storativity, deviatoric fluid pressure, CO₂ and brine viscosity, density and compressibility were also considered. Like Nicot (2008), this model assumed that CO₂ does not dissolve in groundwater and react with the reservoir, as does the Eclipse 100 model of Juanes et al. (2006). However, additional parameters such as permeability anisotropy, trapped gas saturations, geological heterogeneity, and salinity variation were considered by Juanes et al. (2006) during their reservoir simulation investigation of CO₂ capillary trapping and permeability hysteresis. CO₂ was still assumed to remain supercritical and not dissolve in groundwater.

In terms of geochemistry-mass transport coupled software, TOUGHREACT, GEM (Generalized Equation of State Model Reservoir Simulator), and ECLIPSE have all been widely used in reservoir-scale modelling and simulation for CO₂ sequestration (cf. Alexander and Bryant, 2009; Juanes et al., 2006; Xu et al., 2011). GEM is a full Equation of State compositional reservoir simulator. Based on a black oil simulator, GEM has been considerably extended to include both some geochemical and geomechanical constituents, and has been frequently used for simulating CO₂ sequestration (Alexander and Bryant, 2009). Developed by Schlumberger, ECLIPSE has similar functions as GEM, but seems to be less explored for CO₂ sequestration modelling.

Other multicomponent reservoir simulators such as METSIM2 have also been used to model CO₂ behaviour in a geosequestration reservoir, but more work is needed for such environments to be adequately described (Shi et al., 2011).

Given that CO₂ does dissolve in groundwater and react with formations, and there can be a considerable difference in the density and hence volume of a given mass of liquid CO₂ in comparison with supercritical CO₂, in a real reservoir there is potential for alteration of geomechanical properties which could lead to fracturing in spite of injection pressure being less than lithostatic. Some models such as the CHEARS reservoir-scale CO₂ behaviour model of Flett et al. (2005) do consider the range of CO₂ solubility, irreducible water saturation, CO₂ non-ideality and PVT correlations. However, no geochemical reactions were incorporated into their modelling study. Whilst the reservoir modelling approach taken by our group in the current ANLEC study is likely to be similar to that of Flett et al. (2005) in terms of CO₂ behaviour description, geochemical reactions will also not be directly incorporated into the particular model. Instead, geochemical effects will be separately modelled, as will geomechanical effects of CO₂, and then this will be integrated into the performance of the reservoir-scale model.

Many efforts have been made to couple the effect of CO₂ injection on geomechanical behaviour. For example, a mechanical earth model MEM and wellbore stability analysis executed by Lee et al. (2009) for a CO₂ injection well in Eau Claire shale showed that the injection well suffered from a severe borehole enlargement. To obtain zonal isolation and containment, injection well enlargement had to be minimized.

Arsyad et al. (2011) have coupled hydromechanical FLAC3D model with TOUGH2 to study the hydraulic behaviour of their rock samples.

Eshiet and Sheng (2011) used the discrete element model DEM to dynamically capture the geomechanical responses of a reservoir system as a result of drag forces and pressure build-up from the injected fluid CO₂.

3.3. Multiscale-coupled models

The simulation of nonlinear processes such as thermal flow, pressure influence, solution transport, chemical reactions on matrix surfaces, and variation of heterogeneous material structure in subsurface systems is challenging because of the inherently complex morphology of such complicated and disordered porous media coupled with multi-physicochemical transport and interfacial processes.

Complicated fluid phenomena such as inter-phase reactions, phase separation, pore characteristics, capillary pressure, interfacial tension and surface wetting exist in most common cases of multicomponent and multiphase systems (Bennion and Bachu, 2005, 2006a,b).

Subsurface flows are usually described from the perspective of macro-scale view by solving conservation equations (e.g. mass, momentum and energy), conventionally by numerical methods such as the finite volume, finite difference and finite element method (Joseph et al., 1981; Nithiarasu et al., 1997). The representative elementary volume (REV) concept has been applied broadly in the macro-scale simulation of subsurface flow in heterogeneous porous media. In these applications, the flux densities and the potential gradients of the fluid phases are related by relative permeability (Onsager transport coefficients (Onsager, 1931), including coupling coefficients that rely on the fluid volume fractions in the representative elementary volume).

Conventionally, such material parameters (e.g. porosity and permeability) in each representative elementary volume are defined based on the experiments as well as statistical correlations, and are then averaged and upscaled to the grid blocks used in field scale or reservoir scale simulation. However, multicomponent and multiphase fluid flow generally shows hysteretic behaviour that is difficult to rigorously represent with simple relative permeability models (Bear, 1988).

The classical methods for solving nonlinear multiscale processes employ the explicit introduction of different coordinate systems into the governing continuum equations (Cohen and Rosenblat, 1979), during which the characteristic scale parameters of the coordinate systems under different scales are applied to derive the governing equations for each scale (Kouznetsova et al., 2004; Pasternak and Mühlhaus, 2005; Yu and Fish, 2002). However, classical multiscale methods are only applicable for periodic microstructures and weak interactions between different scales.

Compared with the methods mentioned above, up-scaled methods show similar capability in application of weak interactions between different scales, but are not suitable for problems with random coefficients (Chen et al., 2003). The same applies for asymptotic homogenization theory-based multiscale models (Morandi Cecchi and Fornasier, 2005; Zhang et al., 2007) that are widely employed to analyze composite materials and poroelastic materials with periodic structures.

Using conventional methods, some macro-scale geo-fluid phenomena, such as fluid flow with very large density and viscosity ratios, can be numerically simulated and predicted efficiently (e.g. Connor and Brebbia, 1976; Huyakorn and Pinder, 1986; Krause, 1997; Lewis et al., 2004; Peyret and Taylor, 1985; Reddy and Gartling, 2010). However, the shortcoming of these methods is that they ignore the detailed characteristics and variation of the heterogeneous structure and matrix properties at the pore scale, where complex nonlinear geo-fluid dynamics take effect. Thus, we intend to incorporate pore- and mineral-network micro-CT scanning analysis, and QEMSCAN mineral distribution maps, into our models. As traditional homogenization theories cannot be directly applied to heterogeneous porous media, it is essential to propose new methodologies to directly model the coupled nonlinear pore scale processes in heterogeneous porous media and further evaluate the material parameters (i.e. 4D permeability) for macro-scale simulation of subsurface systems.

It is thus imperative to understand complex fluid-mechanics at the pore scale, measure the variation of pore scale heterogeneous structure and material properties, and build correlations of variables at the pore scale and also the macro-scale.

3.3.1. Pore scale modelling – a Lattice Boltzmann approach

We have selected the Lattice Boltzmann method (LBM) to simulate the detailed reactive transport phenomena at pore scale. The Lattice Boltzmann method is regarded as one of the most applicable methods for modeling laminar to turbulent flow of complex fluid (Succi, 2001; Sahimi, 2011). By simulating streaming and collision processes across a limited number of particles, the intrinsic particle

interactions evince a microcosm of viscous flow behaviors applicable across the greater mass (Qian et al., 1992; Sukop and Thorne, 2006). Compared with other numerical methods such as molecular dynamics, dissipative particle dynamics and the pore network method, the Lattice Boltzmann approach has shown extensive applicability to the meso-scale simulation of complex nonlinear coupled processes, and multicomponent/multiphase flow such as phase separation, cavitations, solute transport, chemical reactions, evaporation and fluid interactions with surfaces, as well as fluid flow through complex domain geometries (e.g. Shan and Chen, 1993; Chen and Doolen, 1998; Succi, 2001; Wolf-Gladrow, 2004; Sukop and Thorne, 2006). The flexibility and relative ease-of-implementation make it an attractive option to solve a range of computational fluid dynamics and nonlinear coupled processes problems in geosciences.

The capability of LBM in modeling nonlinear physical processes in heterogeneous and fractured porous media includes:

- 1) Heterogeneity description: To implement the approximation of heterogeneous structure and distinguish the pores/fractures with porous matrix, a pore/solid model is employed that there can be either 0 or 1 for solid particle at a lattice node (1 for impermeable matrix and 0 for pores/fractures), with which heterogeneity in the porous media can be simply represented (Guo and Zhao, 2002; Xing et al., 2011). To simulate boundary conditions, values in macroscopic scales can be directly employed to drive the flow such as pressure and velocity (Ziegler, 1993; Chen et al., 1996; Zou and He, 1996; Zhao-Li et al., 2002).
- 2) Interface interactions: To describe the effects of internal and external forces on the geo-fluid system, some models (Buick and Greated, 2000; Guo and Zhao, 2002) have been developed, which will be essential to model the surface conditions between different components and phases, fluid interactions and effects with the disordered porous media. In multicomponent and multiphase geo-fluid simulations, the most popular approach, the Shan-Chen theory (Shan and Chen, 1993; 1994) considers that the internal force behavior is attractive in a single-component multiphase fluid and repulsive in a multi-component immiscible fluid. The fluid-solid interactions and the wetting behavior based on molecular interaction concepts have also been captured in the Shan and Chen approach.
- 3) Geochemical reactions: To model the geochemical processes including dissolution and precipitation on rock surfaces and chimney structures at seafloor hydrothermal vents, the effect of fluid flow on the chemical reaction at solid surfaces was studied by Chen et al. (Chen et al., 1995), and similar research on the effect of nutrient diffusion and flow on coral morphology was carried out by Kaandorp et al. (Kaandorp et al., 1996). A set of reaction diffusion equations advected by velocities governed by the Navier-Stokes equation have also been discussed by Dawson et al. (Dawson et al., 1993), which has been used to study the effective diffusivity of a heterogeneous medium when the inclusion was impermeable or permeable with a different diffusivity (Alvarez-Ramírez et al., 1996; Chen and Doolen, 1998).
- 4) Transport of multicomponent solutes and multiphase fluid: To describe solute transport, two approaches are frequently used in discrete pore/solid systems: i) Defining one component as a solute by eliminating the non-local interactions between the geo-fluid components, in which the solute component is coupled with the fluid component as usual for multicomponent and multiphase, although with small or zero non-local interaction (Shan and Chen, 1993; 1994; Chen and Doolen, 1998). In this approach, the solute is considered an active solute component, and the densities of the solute and solvent are complementary (e.g. an increase of solute concentration is accompanied by a decrease in solvent concentration, ii) Defining the second component as a passive solute, in which the solute component is considered as passive, having no velocity of its own, and is carried along by the solvent (Yoshino et al., 2009). Several models have been proposed in the past two decades with examples ranging from simple diffusion to buoyant mixing of dense solutions (Perea-Reeves and Stockman, 1997; Stockman, 1997). Other

models have been employed to simulate mineral dissolution and precipitation as well (Kang et al., 2004), and models and applications with more general and more complex interfacial (heterogeneous) chemistry have been utilized to simulate pore scale reactive transport (Maier et al., 2000; Knutson et al., 2001; Zhang and Kang, 2004; Kang et al., 2006; Kang et al., 2007). These models will be useful in applying to address the CO₂ geosequestration problem.

3.4. Summary and analysis

Modelling is expected to provide predictive capability for risk assessment and operational guidance. Therefore, the predictive capacity of the model is of great importance, which relies on a sound model framework and accurate rock and fluid parameters. The multiscale nature of the CO₂ injection process into sandstone formation demands a multiscale modelling approach, which couples meso-scale modelling (centimetre scale) with macroscopic simulation (kilometre scale), in order to capture the process dynamics and the heterogeneity. The meso-scale modelling and simulation is expected to feed the 4D permeability, porosity, dissolution and precipitation rates to the macro-scale models.

The task of linking the two length-scale models is not trivial. For example, the permeability change on the centimetre scale is very likely to be more variable than it on the metre scale or kilometre scale. Therefore, the meso-scale simulation results not only require validation against the corresponding experimental data, but also validation against available field-study data for adjustments. The accuracy requirement also demands a large number of simulations at the meso-scale, in order to capture the heterogeneity nature of the sub-formation. A stochastic approach will need to be employed to translate the meso-scale simulation results to parameters that are sensible and useful in the macroscopic models.

4. Co-contaminants SO_x, NO_x and O₂ in CO₂ streams

CO₂ captured from flue gas (e.g. coal fired power stations) will contain up to a few percent of co-contaminants such as SO₂, O₂, N₂, Ar, NO_x, H₂S, and H₂O. The cost of carbon capture and separation, and hence storage can be reduced if CO₂ can be stored safely together with these co-contaminants. Acid gas injection with the co-contaminant H₂S has been demonstrated safely in Canada for many years (Bachu, 2005).

Injecting CO₂ containing SO₂, O₂ and NO₂ results in formation of acids stronger than carbonic acid, (e.g. sulfuric, sulfurous and nitric acid) reducing formation water pH to as low as 0-1, and has the potential for increased mineral dissolution compared to pure CO₂ injection, and hence increased cation release and reservoir porosity in the short term. This may provide conditions for enhancing CO₂ solubility and mineral trapping in the longer term. Additionally, the presence of compressible gases such as SO₂ can increase storage capacity. Laboratory experimental and modelling studies of co-contaminants (with the exception of H₂S) applicable to sandstone systems are extremely lacking.

Geochemical modeling studies relevant to sandstone sequestration with 1% SO₂ co-injection have indicated formation water pH reduction to zero in an acidified zone around the well bore, and reduction of iron from iron bearing minerals (Xu, 2007, Knauss, 2005, Gunter, 2000, Palandri, 2005). Outside the acidified zone, carbonate minerals including siderite and dolomite precipitated sequestering CO₂ and reducing porosity (Palandri, 2005; Bacon, 2009).

Three batch experimental studies of SO₂ co-injection relevant to sandstone sequestration indicate: Fe^{III} in hematite was reduced to Fe^{II}, trapping CO₂ as siderite after 611h, with metastable pyrite formation (Palandri and Rosenbauer et al. 2005). Hematite conversion to metastable pyrite and elemental S occurred after 17h, followed by precipitation of siderite, dawsonite (derived from kaolinite in the parent material) and iron sulphate after 264 h. Small amounts of kaolinite were more altered than hematite

(Garcia et al. 2011). Goethite conversion to siderite occurred in a shorter time period (576h) than the equivalent conversion of hematite (Garcia et al. 2012).

Kummerow et al. (2011) treated Stuttgart Formation rock with 1% SO₂ in CO₂ and showed a decrease in permeability and increase in electrical resistivity indicating framework alterations and redistribution of fines. In laboratory batch experiments, pure minerals reacted with 0.5% SO₂ or NO₂ injected in CO₂ and highly saline brine (3M NaCl to represent German basin conditions) showed significant dissolution with mobilization of cations (especially calcium) up to 10 times that with pure CO₂ (Wilke, 2012). Anhydrite was also converted to gypsum which is less dense, and mineral transformations such as this could potentially self-seal overlying cap rocks in reservoirs. In a laboratory batch reactor study of CO₂ injection with 4% SO₂ and 4% O₂ into a water-carbonate system, Renard et al. (2011) observed almost 100% dissolution of pyrite and calcite, and mineral alteration 10 times that observed with pure CO₂. Schaefer and co-workers (2012) observed hannebachite (CaSO₃) formation on carbonate minerals exposed to wet scCO₂ in low water environment batch experiments.

Co-contaminant experiments at CO₂ storage conditions have been limited to SO₂ (and H₂S not documented here). Further experiments with the co-contaminant NO₂ are needed, as are integrated studies of the geochemical and physical effects of the co-contaminants SO₂, NO₂, and O₂ on Australian sandstone samples. Actual flue gas compositions of impure CO₂ will contain orders of magnitude less SO₂ than the above experiments, e.g. 4 % SO₂ used in previous experiments would be approximately 40000 ppm which is not realistic (see Table 3).

Table 3: CO₂ stream composition of impurities (Kather, 2009; IEAGHG 2011), and DYNAMIS limits (de Visser 2008). Liu (2010), and Sass (2009), predict SO_x and NO_x levels from an oxyfuel plant may actually be orders of magnitude higher. Other impurities not shown here include N₂, Ar, and CO.

Gas	Post combustion			Oxyfuel			Dynamis
	Comp. 1	Comp. 2	Comp. 3	Comp. 1	Comp. 2	Comp. 3	
CO ₂ (vol%)	99.93	99.92	99.81	85.00	98.00	99.94	>95.5
O ₂ (vol%)	0.02	0.02	0.03	4.70	0.67	0.01	<4 Δ
H ₂ O ppm	100.00	100.00	600.00	100.00	100.00	100.00	500.00
NO _x ppm	20.00	20.00	20.00	100.00	100.00	100.00	100.00
SO ₂ ppm	10*	10*	20*	50.00	50.00	50.00	100*
SO ₃ ppm				20.00	20.00	20.00	

* SO₂+SO₃, Δ EOR 100 - 1000ppm as lack of experiments on effects of O₂

SO_x in flue gas is actually in the range 10 – 70 ppm depending on the source, NO_x levels will be in the range of 20 - 100 ppm, and O₂ will be more abundant with a wide range of possible values including 0.015 (post combustion capture) to 5% (oxyfiring) (IEAGHG, 2011). Nitrogen and argon amongst others will also be present in the ranges 0.01 – 6%, and while not reactive they change physical properties such as storage capacity. The combination of co-contaminants present in actual flue gases will lead to different reactions and levels of corrosion. Higher O₂ levels will lead to oxidizing conditions, and oxidation of SO₂ to sulphuric acid (catalyzed by NO_x), whereas at low O₂ levels less corrosive sulfurous acid may form. Laboratory batch reactor experiments and modeling of CO₂ storage with co-contaminants has so far been mainly limited to pure mineral studies measuring either geochemical or physical effects often with one co-contaminant gas present. Mineral assemblages present in natural reservoir and seal rock present potential for new site specific combination reactions compared to pure minerals such as precipitation of clay coatings on rock surfaces, reducing porosity, reactivity, and preventing CO₂ movement. Hence, reactions can be highly dependent on the reservoir mineralogy and additionally on formation water salinity.

Only one co-contaminant reaction experiment has focussed on the wet scCO₂ phase reactions of sandstone minerals, as opposed to bulk water reactions, even though wet scCO₂ has been suggested to

be more reactive, and is the phase present in contact with sealing caprock (e.g. Loring 2011; Shao, 2012). Future experiments with co-contaminants in wet scCO₂ are needed, especially for caprock which will be in contact with a wet scCO₂ phase which is buoyant.

Integrated experiments to determine geochemical and permeability effects of CO₂ injection with flue gas levels of co-contaminants on characterized geosequestration target reservoir rock and seals, with both geochemical and multiphase fluid flow modeling are needed in the future.

Piping and well materials such as steel and cement are more susceptible to corrosion at low pH conditions induced by CO₂ and co-contaminant injection, therefore the testing and selection of appropriate types e.g. high alloyed steel vs carbon steel according to laboratory experiments is also necessary in the future. In batch experiments in the wet scCO₂ phase, Choi et al. (2010) observed that addition of 2, and 4 % O₂ to CO₂ significantly increased the corrosion rate of pipeline steel over 24h. 1% SO₂ dramatically increased the corrosion rates from 0.38 to 5.6 mm/y and it increased further to 7 mm/y upon addition of both O₂ and SO₂. The formation of a layer of precipitated non porous calcite on cement has been observed in lab leaching experiments with acid gas H₂S co-injection to amour the cement from further corrosion (Jacquemet, 2012). However leaching and flow through experiments on well materials with impure CO₂ containing flue gas mixes of SO₂, O₂ and NO₂ are also necessary.

5. Summary

This review focused on geochemical and geomechanical experiments and associated models reported in the literature relevant to geosequestration of CO₂ in sandstone, supporting ANLEC Project 3-1110-0101.

This project encompasses three key parts, aimed at supporting CO₂ geosequestration field demonstration/commercial projects: Part 1, geochemical reaction investigations of the CO₂-H₂O-rock system of target host formations, identifying changes to mineralogy, porosity and permeability; Part 2, measurements of 3D mechanical properties and 3D/4D permeability, investigating their dynamic changes over reaction time; Part 3, advancing development of physical and numerical models, to replicate the lab findings of fluid and mass transport, for application at different spatial and temporal scales.

Most lab-scale geochemistry studies have used batch reactors, which rely on soaking solid samples over extended periods and then examining the changes to the fluid and/or the solid material. A smaller number of studies have used continuous flow reactors. In both cases, outcomes with respect to observed mineralogy changes have been mixed, mainly corresponding to the complexity of the system being probed. General observations are that calcite and dolomite cements are dissolved, unstable clays like smectite may react, and feldspar minerals are variably etched with precipitation of clays and ferroan carbonates/oxy-hydroxides observed in many of the longer term experiments. In some cases it is not clear whether the precipitates formed under ambient conditions in the reactor or during depressurization of the system. A related problem is one of analysis of the system under realistic conditions. While the experiment may be conducted under high pressure and temperature conditions, sample chemical analysis is virtually always done at ambient pressure, which changes the outcomes.

Many geochemistry modelling studies have used various computer programs based on principles of thermodynamics or mass transport to model chemical equilibrium under new transient conditions after a disturbance, and some even incorporate chemical kinetics. Modelling is expected to provide predictive capability for risk assessment and operational guidance. Therefore, the predictive capacity of the model is of great importance, which relies on a sound model framework and accurate rock and fluid parameters. The multiscale nature of the CO₂ injection process into sandstone formation demands a multiscale modelling approach, which couples meso-scale modelling (centimetre scale) with macroscopic simulation (kilometre scale), in order to capture the process dynamics and the heterogeneity. The meso-

scale modelling and simulation is expected to feed the 4D permeability, porosity, dissolution and precipitation rates to the macro-scale models.

The task of linking the two length-scale models is not trivial. For example, the permeability change on the centimetre scale is very likely to be more variable than it on the metre scale or kilometre scale. Therefore, the meso-scale simulation results not only require validation against the corresponding experimental data, but also validation against available field-study data for adjustments. The accuracy requirement also demands a large number of simulations at the meso-scale, in order to capture the heterogeneity nature of the sub-formation. A stochastic approach will need to be employed to translate the meso-scale simulation results to parameters that are sensible and useful in the macroscopic models.

6. Tables of laboratory and modelling experiments

Table 1: Geosequestration laboratory experiments

Paper	Study type*	Samples		Water type	Sample characterisation techniques	Techniques for analytical analysis of experiments	Experiment parameters	Experimental set-up type	Pertinent observations of experiments
		Rocks	Minerals						
Gunter <i>et al.</i> (1997)	Exp & Mod	Galuconitic sandstone	Major labradorite, albite, biotite, quartz. Minor K-feldspar, glauconite, kaolinite, calcite, dolomite, siderite	Artificial bicarbonate brine	XRD, SEM, grain-size sieve analysis	XRD, SEM, ICP-OES, ion chromatography, titration	P, T, month-long timeframe, powdered samples	Autoclave	No significant change in mineralogy, increase in alkalinity of water, some increase in K levels in water
Shiraki and Dunn (2000)	Exp	Sandstone	Feldspar, anhydrite, kaolinite, others	Artificial brine	Porosity & permeability measured by CMS-300 machine, SEM, standard petrography	Titration, ICP-OES, ion chromatography, porosity & permeability measured by CMS-300 machine, SEM, standard petrography	pCO ₂ 166 bars, T 80C, 160 hr duration,	Core-flood, with fluid samples analysed periodically	Variable porosity changes (neg to 44% incr), partial dissolution of mins such as feldspar and anhydrite, kaolinite precipitation, decrease in perm of some cores that didn't show porosity change.
Kaszuba <i>et al.</i> (2003)	Exp	Sandstone, shale	Quartz, oligoclase, microcline, biotite, sericite, calcite, minor others	Artificial brine	XRD, SEM-EDS	ICP-OES, ICP-MS, SEM-EDS	200 C, 200 bars, 59 days, rock chips	Batch reactor, with small fluid samples able to be taken periodically.	Magnesite precipitation, etching of silicate minerals
Krumhansl <i>et al.</i> (2003)	Exp & Mod	Sandstone	Carbonates, albite, K-feldspar	Natural formation waters	XRD, SEM-EDS	Ion Chromatography, ICP-OES, ICP-MS, SEM-EDS, XRD	P 48 atm, T 40 C, 6.5 & 19 mth timeframe	Rock chips in autoclave	Plagioclase corroded but K-feldspar didn't, clay precipitation, carbonate cement dissolved

Paper	Study type*	Samples		Water type	Sample characterisation techniques	Techniques for analytical analysis of experiments	Experiment parameters	Experimental set-up type	Pertinent observations of experiments
		Rocks	Minerals						
Kaszuba <i>et al.</i> (2005)	Exp	Sandstone, shale	Quartz, oligoclase, microcline, illite, biotite, sericite, calcite, minor others	NaCl brine	Standard petrography, SEM, XRD, XRF	ICP-OES, ICP-MS, standard petrography, SEM-EDS, SEM-BSE imaging	200 C, 200 bars, 32 days brine and rock chips, then 45 days with CO ₂ , or 77 days only brine and rock	Batch reactor	Magnesite and siderite precipitation from CO ₂ -brine expts, etching of silicate minerals and partial or total dissolution of some minerals like calcite
Rosenbauer <i>et al.</i> (2005)	Exp	Sandstone, limestone	Quartz, oligoclase, K-feldspar, kaolinite, calcite	Artificial & natural brine	Well log info	XRD, ICP-OES, ICP-MS, Ion Chromatography	25 to 120 C, 100 to 600 bars	Autoclave, fluid samples able to be periodically taken	Ionic species concentrations changed non-linearly over time, some porosity increase but this often was off-set by precipitation of minerals like anhydrite during CO ₂ desiccation of the samples.
Sorai <i>et al.</i> (2005)	Exp	N/A	Feldspar (anorthite)	Deionised water	AFM	DIM, AFM	T 25, 50, 65, 80 C, pCO ₂ 10 Mpa	Large crystal cleavage fragments in batch reactor	Dissolution rates estimated on basis of height diffs between reacted and unreacted surfaces
Kaszuba <i>et al.</i> (2005)	Exp	Sandstone, shale	Quartz, oligoclase, microcline, illite, biotite, sericite, calcite, minor others	NaCl brine	Standard petrography, SEM, XRD, XRF	ICP-OES, ICP-MS, standard petrography, SEM-EDS, SEM-BSE imaging	200 C, 200 bars, 32 days brine and rock chips, then 45 days with CO ₂ , or 77 days only brine and rock	Batch reactor	Magnesite and siderite precipitation from CO ₂ -brine expts, etching of silicate minerals and partial or total dissolution of some minerals like calcite

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		Rocks	Minerals						
Rosenbauer <i>et al.</i> (2005)	Exp	Sandstone, limestone	Quartz, oligoclase, K-feldspar, kaolinite, calcite	Artificial & natural brine	Well log info	XRD, ICP-OES, ICP-MS, Ion Chromatography	25 to 120 C, 100 to 600 bars	Autoclave, fluid samples able to be periodically taken	Ionic species concentrations changed non-linearly over time, some porosity increase but this often was off-set by precipitation of minerals like anhydrite during CO ₂ desiccation of the samples.
Sorai <i>et al.</i> (2005)	Exp	N/A	Feldspar (anorthite)	Deionised water	AFM	DIM, AFM	T 25, 50, 65, 80 C, pCO ₂ 10 Mpa	Large crystal cleavage fragments in batch reactor	Dissolution rates estimated on basis of height diffs between reacted and unreacted surfaces
Bertier <i>et al.</i> (2006)	Exp	Sandstone	K-(Na)-Feldspar, illite, smectite, chlorite, kaolinite, quartz, ankerite/dolomite, siderite, haematite grain coatings	Artificial brine	Standard petrography, XRD, He-pycnometry, image analysis, SEM-EDS&BSE, EPMA	XRD, SEM-EDS	80 C, 150 bars, 8 month duration	Cores in batch reactor	Dissolution of carbonates, alteration of Al-silicates, potentially some precipitation of minerals but difficult to tell with certainty if it's not just detrital material washed out of the cores
Sorai <i>et al.</i> (2007)	Exp	N/A	Feldspar	Deionised water	Phase-shift interferometer	Phase-shift interferometer	25 C, 50 C, 80 C, pCO ₂ 10 Mpa, sample removed from cell and washed with H ₂ O before air drying every 6 hrs & observed,	batch reactor	Differential interference microscope (DIM) images show progressive etching of feldspar surface, more precise measurement of reactive surface area intended to improve reaction rate calculations

Paper	Study type*	Samples		Water type	Sample characterisation techniques	Techniques for analytical analysis of experiments	Experiment parameters	Experimental set-up type	Pertinent observations of experiments
		Rocks	Minerals						
Wigand <i>et al.</i> (2008)	Exp & Mod	Sandstone	Quartz, K-feldspar, albite, illite, dolomite, mica, minor others	NaCl brine	XRD, SEM-EDS, EMPA, porosity, permeability	ICP-MS, ICP-OES, SEM-EDS, EMPA	30 Mpa confining pressure, pore pressure 15 Mpa, scCO ₂ injected at 1-2 Mpa gradient, 1496 hr timeframe, 60 C, periodic sampling of fluids	Autoclave	K-feldspar, albite corrosion, dolomite dissolution, montmorillonite precipitation, illite kaolinite quartz not affected
Ketzer <i>et al.</i> (2009)	Exp & Mod	Sandstone	Quartz, K-feldspars, minor plagioclase and others	Deionised water	SEM-EDS	SEM-EDS	Dry ice, deionised water, 10 to 15 Mpa, T 200 C, 100 hr timeframe.	Batch reactor	Opal and carbonate precipitation
Bacci <i>et al.</i> (2011)	Exp & Mod	Limestones	Calcite, minor quartz	Saline	XRD, porosimetry, pycnometry	ICP-OES	T, P, pH, salinity, whole-core samples	2 cores in cells of diff P&T conditions, connected in series	Formation of "worm holes" through samples
Rimmelé <i>et al.</i> (2010)	Exp	Sandstone, limestone	Calcite, quartz, feldspar, clay, mica, minor others	Deionised water	Physical dimensions, weight, photography, Young's modulus, Poisson's ratio, H ₂ O permeability, Hg-porosimetry, XRD, standard petrography, SEM-EDS, SEM-BSE imaging	Physical dimensions, weight, photography, Young's modulus, Poisson's ratio, H ₂ O permeability, Hg-porosimetry, XRD, standard petrography, SEM-EDS, SEM-BSE imaging, Raman spectroscopy	90 C, 28 Mpa, month timeframe, samples pre-soaked in DI water for 2 days to ensure total pore saturation	Autoclave with cores	Mechanical properties unaffected, slight increase in permeability, decreased weight & density with increased porosity, not much change in pore size distribution, no significant change in mineralogy

Paper	Study type*	Samples		Water type	Sample characterisation techniques	Techniques for analytical analysis of experiments	Experiment parameters	Experimental set-up type	Pertinent observations of experiments
		Rocks	Minerals						
Scislewski and Zuddas (2010)	Exp & Mod	Mafic	Albite (70%) and 30% other mafic minerals. Albite (75%), microcline (10%), quartz (5%), biotite (5%), calcite (3%), muscovite (<1%), others (<2%)	Deionised water	XRD, SEM, standard optical petrography	Flame or flameless AAS, microcolorimetry, anionic chromatography, titration, SEM	5% CO ₂ 95% air mixture + dionized water, constant T (22 C), atm P, pH 4.56, constant flow rate	Glass column with filter, and in-put flow from micro-pump, continuous flow	SEM after exps revealed growth of alteration minerals over grains
Zemke <i>et al.</i> (2010)	Exp	Sandstone	Not specified	Artificial formation water	NMR (petrophysical parameters, porosity, pore radius distribution), He-pycnometry, Hg-porosimetry, permeability	NMR (petrophysical parameters, porosity, pore radius distribution)	T 40 C, P 6 Mpa, timeframe 6 mths. T 40 C, p CO2 5.5 Mpa, 15 mths timeframe.	Batch reactor	Slight increase in porosity and more large pores
Heeschen <i>et al.</i> (2011)	Exp & Mod	Unspecified	Carbonates, feldspars, micas, clays, "Fe-minerals", (quartz?)	Artificial brine	EPMA, SEM-EDS, XRD, XRF, ICP-OES, ICP-MS	EPMA, SEM-EDS, XRD, XRF, ICP-OES, ICP-MS	T 120 C, P 200 bar, 160 hr timeframe	Cores in batch reactor, fluid samples taken periodically	Some mineral dissolution, iron precipitation on dolomite surface
Labus and Bujok (2011)	Exp & Mod	Sandstone, mudstone	Quartz, K-feldspar, siderite, muscovite, albite, kaolinite, annite, illite, montmorillonite, calcite, anorthite, phlogopite, beidelit, gypsum	Brine?	Standard petrography, XRD, Hg-porosimetry, He-pycnometry	SEM-EDS	40 C, 75 days, P 70 - 125 bars, pCO2 47 to 68.5 bars	Autoclave	Mineral etching, K-regions more etched than Na in feldspar, clay & dawsonite precipitation

Paper	Study type*	Samples		Water type	Sample characterisation techniques	Techniques for analytical analysis of experiments	Experiment parameters	Experimental set-up type	Pertinent observations of experiments
		Rocks	Minerals						
Lima <i>et al.</i> (2011)	Exp	sandstone, shale	Quartz, albite, anorthite, magnesium calcite, dolomite, illite, I/S, kaolinite, chlorite	NaCl brine	XRD, SEM-EDS, TEM-EDX	XRD, SEM-EDS, TEM-EDX, ICP-OES	80 C, supercritical or atm P CO ₂ , 3 to 6 mths, 0 to 12 Mpa,	Batch reactor, either pressurize or at atm P	After 6 mts, possible reaction of parts of I/S indicated by XRD, SEM showed partial dissolution of feldspar mins, TEM suggested newly crystallized illite in I/S structure (due to S rxn)
Shi <i>et al.</i> (2011)	Exp & Mod	Sandstone	not specified	Artificial brine	X-ray CT, Hg-porosimetry	X-ray CT	T 40 C, P 10 Mpa,	Core flood continuous flow	Porosity heterogeneity has big impact on flow pathway/s of CO ₂

* Exp – Experimental, Exp & Mod – Experimental and Modelling

Table 2: Geosequestration geochemical modelling studies

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parameters	Pertinent model assumptions	Other notes
Gunter <i>et al.</i> (1997)	Exp & Mod	Water chemistry	PATHAR.94	Geochemical reactions	Dissolution & precipitation of quartz, K-feldspar, albite, anorthite, annite, kaolinite, calcite, dolomite, siderite	50 yr average timeframe, mineral reaction rate constants, activation energies, reactive surface area of mineral grains, initial alkalinity measured during experiments		
Krumhansl <i>et al.</i> (2003)	Exp & Mod	Geochemistry	REACT, EQ3/6	Reaction-path modelling	Various			Simply in-putting brine compositions results in the program/s suggesting the presence of minerals that are not actually present in the samples.
Kirste <i>et al.</i> (2004)	Exp & Mod	Geochemistry	PREEQC, GWB	Former for ion speciation & pH, GWB for kinetics & equilibrium based rxn path geochem models	Formation of kaolinite, quartz, siderite, illite, magnesite, ankerite. Reaction of albite, anorthite, Fe- and Mg- chlorite, K-feldspar	Surface roughness factor, T, pCO ₂ , stoichiometric mineral compositions, synthetic brine composition, water-rock ratio, 70 day, 20 yr or 1000 yr timeframe		
Soong <i>et al.</i> (2004)	Exp & Mod	Geochemistry	PHREEQC	Brine carbonation	Carbonate precipitation	T, pCO ₂ , salinity	Ideal gas law assumed to be adequate, and the expressions to account for non-ideality of brine solution don't apply to high ionic strength used in exps.	

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parameters	Pertinent model assumptions	Other notes
Xu <i>et al.</i> (2004a)	Mod	Geochemistry, Reactive transport	TOUGHREACT	1D, 2D, 3D porous and fractured media, chemical and physical heterogeneity, liquid, gas, solid phases, fluid flow relative to pressure and gravity, capillary pressure effects for liquids, diffusive convective and conductive heat flow. Advection and molecular diffusion, hydrodynamic dispersion. CO ₂ activity, fugacity, and solubility. Mineral dissolution and precipitation. P, T, salinity, delta porosity and permeability. Uses SUPRCRT92 thermodynamic data.	Dissolution & precipitation of minerals in samples	Kinetic rate constants and activation energies (many used for non-related minerals), CO ₂ solubility, mineral reactive surface areas, 100,000 yr timeframe.		Dunite (olivine rich) good rock for sequestration (magnesite and siderite), but not abundant, glauconitic sandstone not so good (high glauconite good though - produces ankerite, siderite, minor dolomite and dawsonite), reaction-caused changes in mineral surface area has big impact on reaction times, mineral precipitation reduces porosity.
Xu <i>et al.</i> (2004b)	Mod	Geochemistry	TOUGHREACT		Dissolution & precipitation of various minerals	Kinetic rate constants, T and P		Presence of H ₂ S in carbonic acid makes little difference to mineral reactions, whereas presence of SO ₂ leads to much lower pH.

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parameters	Pertinent model assumptions	Other notes
Knauss <i>et al.</i> (2005)	Mod	Coupled chemical (TST-type) and simplified fluid flow model	CRUNCH (reactive transport code), TOUGH2	Multi-dimensional, multicomponent modelling in porous media. 2D sim of diffusive, dispersive, & advective transport, non-isothermal reaction & transport, multicomponent aqueous complexation, unsaturated transport with aqueous-gas phase exchange, kinetically-controlled mineral precip & diss, multicomponent ion exchange on multiple sites, multicomponent surface complexation on multiple sites with/without electrostatic correction, microbially-mediated reactions, radioactive decay chains, advective transport of solid phases, multicomponent diffusion with electrochemical correction for differences of diffusion coefficients. Can use fixed activity, total concentration, equilibration with mineral or gas phase, as initial boundary conditions. Uses kinetic & thermodynamic EQ3/6 database. TOUGH2 for transport-only CO2 modelling.	Multiple minerals	Isothermal isobaric fully saturated conditions, 2000 yr reaction timeframe Modal mineralogy and abundances of minerals averaged from XRD and petrographic analysis of 12 samples from proposed pilot injection wells. Formation water composition partly based on assay of water from near-by well.	Darcy flow. Uniform spherical grain shape & size, correction factor applied to account for phyllosilicates adequate. Assumed initial aqueous iron in equilibrium with pyrite. SO ₂ eventually oxidised to sulfate.	Investigation of what may happen with co-injection of CO ₂ with SO _x , and H ₂ S. Found that little difference between CO ₂ -only injection & CO ₂ + significant H ₂ S, however; only small amounts of SO ₂ (if ox to sulfate) sufficient to dramatically lower pH.

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parameters	Pertinent model assumptions	Other notes
Xu <i>et al.</i> (2005)	Mod	Geochemistry, Reactive transport	TOUGHREACT		Multiple minerals	4000 psi, 80 C, 4 week timeframe, powdered samples in batch reactor, deionised water, NaCl water		Some evidence for carbonate formation
Xu <i>et al.</i> (2005)	Exp & Mod	Reactive transport	TOUGHREACT	1D, 2D, 3D porous and fractured media, chemical and physical heterogeneity, liquid, gas, solid phases, fluid flow rel to pressure and gravity, capillary pressure effects for liquids, diffusive convective and conductive heat flow. Advection and molecular diffusion, hydrodynamic dispersion. CO2 activity, fugacity, and solubility. Mineral diss and precip. P, T, salinity, delta porosity and permeability. Uses SUPRCRT92 thermodynamic data.	Dissolution & precipitation of various minerals	Kinetic rate constants and activation energies (many used for non-related minerals), CO2 solubility, mineral reactive surface areas, sandstone capped by shale, 100,000 yr timeframe.		Predicts significant dawsonite precipitation, as well as usual carbonates, most of which forming in the sandstone.
Zwingmann <i>et al.</i> (2005)	Mod	Geochemistry	EQ3/6		Dissolution & precipitation of various minerals	pCO2, T, formation P, porosity, reaction kinetics, activation energies, reactive surface area, 200,000 yr timeframe. Target formation water and mineral composition from analyses done as part of study.	reactive surface area assumed to be same for each mineral	Calcite, dolomite, dawsonite precipitation. Presence of more reactive minerals enhances sequestration.

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parametres	Pertinent model assumptions	Other notes
Peters <i>et al.</i> (2006)	Mod	Pore network model		Intended to improve simulation of geochemical processes during sequestration within realistic rock and mineral structures				Intend to upscale model
Ennis-King and Paterson (2007)	Mod	Geochemistry, convection	TOUGHREACT	Geochemical reactions, convective mixing	Calcite-anorthite-cemented sandstone, siliciclastic slow rxn mineralogy, both modelled for diss & precip	100 timescale, permeability, porosity, T, P		Coupled geochemical reactions with convective mixing
Wigand <i>et al.</i> (2008)	Exp & Mod	Geochemistry	PHREEQC	equilibrium calculations of ion speciation & min sat, fluid & min compositions & dissolution & precipitation	Various	60 C, 15 Mpa pCO ₂ , salinity		
Xu (2008)	Mod	Geochemistry	TOUGHREACT	TST, extended DH and Pitzer ion activity models, etc	Dissolution & precipitation of various minerals	NaCl dominated brine, T, 50,000 yr timeframe, reaction kinetics and activation energies.		Recommends Pitzer model for highly concentrated brines.
Kampman <i>et al.</i> (2009)	Nat Ana & Mod	Geochemistry	PHREEQC			Measured formation water cation composition, T, alkalinity, TDIC, O C H & Sr isotopes, pCO ₂ , SI(calcite), and ionic strength	Flow assumed to be homogeneous	Attempted to calculate reaction rates of minerals based upon their distribution in field (drill cores) and ground water composition changes, I think

Paper	Study type*	Model type/s	Model names	Model description	Chemical reactions modelled	Pertinent model parameters	Pertinent model assumptions	Other notes
Ketzer <i>et al.</i> (2009)	Exp & Mod		PHREEQC		Dissolution & precipitation of various minerals	Reaction rates and activation energies, mineral specific surface areas, T, P, 100 hr timeframe		Didn't think carbonates formed during exps were due to carbonate of CO ₂ , rather were re-precip of dissolved carbonates; conditions too high pCO ₂ for mineral trapping to occur during exps.
Scislewski and Zuddas (2010)	Exp & Mod	Geochemistry	PHREEQCi	Fluid saturation wrt ions of specific minerals	min dissolution (albite, microcline, calcite, biotite, quartz, kaolinite, anorthite, muscovite)			Proposed that overall mineral reaction rates depend upon the early-formed alteration coating stability
Heeschen <i>et al.</i> (2011)	Exp & Mod	Geochemistry	PHREEQC and ChemApp					
Labus and Bujok (2011)	Exp & Mod	Geochemistry	GWB			Mineral specific surface area, 100 day or 20,000 yr timeframe, reaction kinetics and activation energies, T, P, formation water composition	Spherical mineral grains	Modelling shows chalcedony should also precipitate
Pham <i>et al.</i> (2011)	Mod	Geochemistry	PHREEQC	Also used TST and BCF theories.	Dissolution & precipitation of various minerals	Kinetic rate constants, 10,000 yr timeframe		Predicts eventual mineral trapping of CO ₂ , question the Dawsonite formation result. Highlight need for experimental data for precipitation rates of carbonates, nucleation rates for most minerals in general, and more clay dissolution rates.

* Exp & Mod – Experimental and Modelling, Mod – Modelling only, Nat Ana & Mod – Natural Analogue Characterisation and Modelling

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