

GHGT-10

Importance of Co-captured Gases in the Underground Storage of CO₂: Quantification of Mineral Alterations in Chemical Experiments

Katja Heeschen^{a,*}, Andreas Risse^a, Christian Ostertag-Henning^a, Susanne Stadler^a^a*Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, D-30655 Hannover, Germany*

Abstract

Carbon dioxide capture and geological storage (CCS) is being developed to reduce the carbon dioxide (CO₂) emissions from anthropogenic point sources, e.g. fossil-fuel power plants, to the atmosphere. To establish CCS technology, it is indispensable to develop a reliable database and geochemical models concerning the geological storage of CO₂, e.g. in saline aquifers, which are to be filled with “overwhelmingly CO₂” (Directive 2009/31/EC). To establish reliable models it is essential to have applicable thermodynamic properties, kinetic data, and a good understanding of the occurring chemical reactions. So far most experiments and existing data apply to pure CO₂ gas instead of the captured CO₂ waste gas that will contain minor amounts of co-captured gases, e.g. O₂, N₂, NO_x, SO_x, CO, H₂, H₂S. Quantitative measures of the chemical alterations due to these accessory gases are scarce.

In the national COORAL project “CO₂ Purity for Separation and Storage”, a number of institutions work towards a better understanding of environmentally and economically feasible concentrations of the accessory gases during capture, transport, injection and storage. The sub-project at BGR focuses on high-pressure and high-temperature (HPHT) experiments to elucidate mineral and fluid alterations and quantify kinetic rates for the mineral–fluid–CO₂–co-injected gas system. An unstirred batch-reactor system allows for four contemporaneous experiments at precisely defined p–T conditions of up to $p \leq 590$ bar $T \leq 350^\circ\text{C}$. Runs are conducted using three components: 1) natural mono-minerals, 2) salt solutions representing brines of deep saline aquifers in Northern Germany and 3) binary gas mixtures of CO₂ plus one accessory gas. All experiments take place in an inert environment, using gold reaction cells with volumes of up to 130 ml, which allow the addition or removal of fluids throughout the experiment without altering the experimental conditions. Further experiments comprise experiments using (1) multi-mineral set-ups in a batch experiment and (2) up to 45-cm-long sedimentary rock cores in flow-through reactors. The latter system is currently under construction, while batch - and capsular - experiments run successfully.

To further optimize the experimental design and to evaluate the experiments the project combines laboratory experiments and numerical simulations, applying the geochemical simulators PHREEQC and ChemApp which will be coupled to OpenGeoSys (OGS) for thermo-hydro-mechanical-chemical (THMC) process simulations.

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1. Introduction

Carbon dioxide capture and geological storage (CCS) is one of the currently discussed carbon mitigation strategies [1]. It includes capture of CO₂ from flue gas streams to form CO₂ streams that consist “overwhelmingly of CO₂” as pointed out in EU Directive 2009/31/EC (23 April 2009). Up to date the exact composition of CO₂ streams is not yet defined and may vary depending on the origin of the gas as well as the capturing process, e.g. [2]. However, it is crucial to define tolerable amounts of co-captured gases, as those gases alter the physical and the chemical behaviour of the CO₂ stream while transported, injected and stored [3, 4]. It is therefore essential to quantify the effect of possible gas mixtures by laboratory experiments to enable long-term numerical simulations.

Regarding the geochemical reactions, laboratory work has been focussing on the reaction of minerals or rocks with pure CO₂, so far leading to a considerable improvement in the quantity and the quality of the database and the coverage of the temperature-pressure range [4]. As research progresses the geochemical - and physical - properties and alterations due to the co-captures gases come into focus [5-10]. So far, H₂S and SO₂ have been receiving most attention among possible co-injected gases including O₂, N₂, Ar, NO_x, SO_x, CO, H₂, H₂S, COS, and CH₄ [11]. Despite those early efforts, the gaps in the database concerning these gases are large; as is the number of reliable geochemical experiments needed to fill them.

In the German COORAL project “CO₂ Purity for Separation and Storage” (www.bgr.bund.de/COORAL; cited August 2010) a number of institutions work towards a better understanding of environmentally and economically feasible concentrations of the accessory gases during capture, transport, injection and storage. The sub-project presented here places its emphasis on geochemical implications for the geological storage in saline aquifers, using high-pressure and high-temperature (HPHT) experiments to elucidate mineral and fluid alterations and quantify reaction rates for the system: mineral – fluid – CO₂ – co-injected gas (X). The focus is on reactions between monominerals and binary gas mixtures (CO₂ + X) using an unstirred batch-reactor system, whereas flow-through reactors serve for semi-quantitative experiments using sedimentary rock cores of up to 45 cm in length. P-T conditions can be as high as $p \leq 590$ bar and $T \leq 350^\circ\text{C}$. To optimize and to evaluate the experiments the project combines laboratory experiments and numerical simulations.

2. Methods

2.1. Pressure Vessels

A total of four pressure vessels provide the outer framework for static HPHT experiments carried out in inert reaction cells made of gold foil (Figure 1); a set-up based on the work of [12, 13]. Pressure and temperature sensors determine the regulation of a highly precise piston pump and ceramic band heaters. Deviations do not exceed $\pm 1^\circ\text{C}$ and ± 1 bar, respectively. The pressure transmitting medium is water, i.e., pressure changes are transmitted to the content of the reaction cell via the high deformability of the thin gold foil forming the cell. Due to this deformability and the comparably large volume of the cell (130 ml), up to 40% of the original solution can be sampled throughout the course of the experiment using high-pressure titanium tubing and valves fitted to the titanium head of the reaction cell (Figure 1). During sampling no pressure changes are induced. The cell is filled with solution and minerals before closure, while the gas is added once the experimental pressure has been adjusted. In case pure CO₂ is added, e.g. the work of “The Duan Group” ([14]; <http://www.geochem-model.org/programs.htm>; cited August 2010) provides the first basis for the density and saturation calculations needed. For mixed gases dissolved in brines these data are missing to a great extent. In order to avoid the minerals settling to the bottom of the cell, they are placed in an inert PTFE bag (mesh width: 70 μm) hanging from the bottom of the titanium closure. There is no stirring or agitation. Because each reactor can only accommodate a single experiment, preliminary tests are carried out using small gold capsules containing solution and mineral, 34 of which can be placed in one reactor. With this method, selections in terms of fluids and minerals can be made and equilibrium conditions defined.

In the course of the project two different types of pressure vessels will be used. Next to the existing batch reactors, a set of flow-through reactors is under construction. The designs of the head of the pressure vessels are similar, allowing for precise p-T control in an inert environment. However, the flow-through reactors provide space for rock cores with a total length of up to 45 cm. Again the pressure is regulated by piston pumps. To protect the pumps from damage, corrosive gases and highly saline brines will be stored and pumped using media separator.

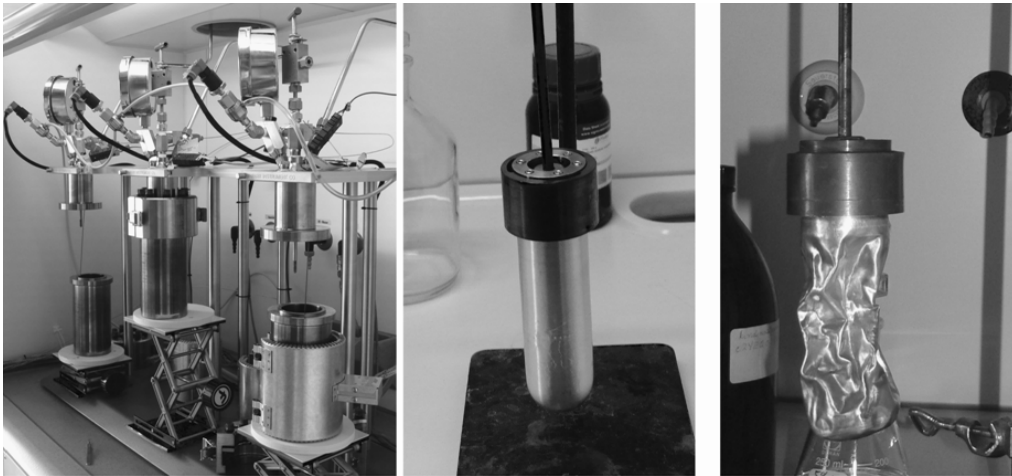


Figure 1 The left-hand panel shows three out of four batch reactors including the pressure vessel (with and without band heater) and the closing device containing the Ti-capillary through which sample fluid can be withdrawn from the flexible reaction cell during the experiment. The reaction cell is shown on the other two panels before (middle) and after (right) an experiment.

2.2 Sample material

The minerals are of natural origin. They are representative for minerals in potential storage formations in Northern Germany, comprising a range of well characterized carbonates, feldspar, micas, clay and iron-bearing minerals. Apart from the clay minerals, crystals are broken down manually and sieved to a grain size of $< 2000 \mu\text{m}$ or smaller, depending on the experiment-specific required grain sizes. Before being used, samples are cleaned with distilled water for five minutes to remove fine material left after grinding (Figure 2). Ultrasonic sound is applied if SEM images before and after do not show any alterations. In terms of batch experiments, the main emphasis is on using mono-minerals for quantitative determination of dissolution rates. Natural rock cores will mainly be placed in the flow-through reactors.

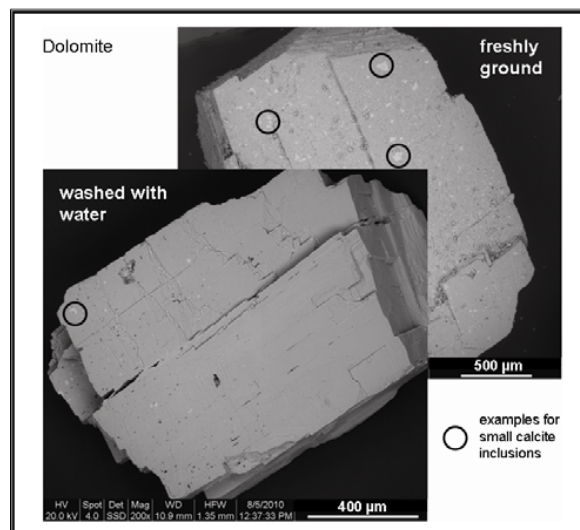


Figure 2 Scanning Electron Microscope (SEM) images of an untreated (back) and washed (front) ground dolomite particle. The light patches are calcite inclusions embedded in the nearly stoichiometric dolomite ($\text{CaMg}(\text{CO}_3)_2$).

Equivalent to the majority of brines in deep saline aquifers of Northern Germany, the salt content of the experimental solutions will vary between 150 and 350 g/l [15]. The prevailing salt will be NaCl, however, experiments with Na-Mg-Ca-Cl brines of similar salinity are envisioned for comparison. At an advanced stage, isotopically labelled fluids are used to substitute some of the gases and simple brines (see 2.3). As for the gases, we use binary mixtures of CO₂ plus one additional gas, the latter being one of the gases possibly found in the CO₂ stream. The concentration of the trace gas to be added will be chosen based on the work of other groups within the COORAL project.

2.3 Measurements

The majority of measurements take place in the laboratories at BGR. The methods to investigate the original and altered minerals include EPMA, SEM EDS, XRD, XRF and wet chemistry. Depending on particle size, the BET method or particle size analysis are applied to determine the mineral surface area. ICP-OES and ICP-MS are used to detect changes in cation and anion concentrations of the solutions. To improve detection limits, methods are being developed that allow measurement of isotopic alterations A) to verify the data gained from conventional methods and B) to quantify reaction rates of less reactive silicates that show very slow dissolution, precipitation and exchange reactions under the given conditions. Thus, part of the experiments will be performed with isotopically-labelled fluids and gases (e.g. ¹³C; ¹⁸O) prepared in the laboratory.

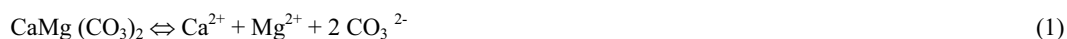
2.4 Modelling environment

The project applies the geochemical simulators PHREEQC [16] and ChemApp [17], which will be coupled to OpenGeoSys (OGS) [18] for thermo-hydro-mechanic-chemical (THMC) process simulations. The aim of the geochemical modelling is to describe chemical alterations of the minerals and of the fluids/gases as a function of the gas injection and to provide additional kinetic data for the temperature and pressure range studied. The THMC modelling will address processes in the natural sedimentary rock cores in the further course of the project.

3. Experimental results

The reactors that consist of an external pressure vessel and an internal flexible cell proved to be very successful in operation as experimental conditions can be achieved very quickly without overshooting; they make it possible to take a rather large number of samples (up to 40 ml) during the course of the experiment, allow sampling without any pressure changes caused to the system, and enable the addition of well defined gas volumes at high pressure as described in [12].

The first set of experiments uses pure CO₂ and carbonates to test the laboratory set-up, fill discrete p-T gaps in the carbonate-CO₂-solution system not addressed in the literature, and adjust the modelling environment. The first of these experiments has just been completed successfully, investigating the dissolution of dolomite in a CO₂-saturated brine. The dissolution reaction is given by



The solid was a nearly pure stoichiometric dolomite (49.6 mol % CaO) with grain sizes of <1000 µm, containing little iron (Fe, 0.58 wt%) and manganese (Mn, 0.15 wt%). The solution had a salt content of 150 g/l NaCl and the solid:liquid ratio was 1:20. Temperature was set to 120°C (15 hours after injecting CO₂) at a pressure of 200 bar over a duration of 160 h (8900 min). The calculated CO₂ volume (after [14]) was added to the reaction cell shortly after the pressure was set to 200 bar. The pH ranged from 5 – 6 under lab temperature and pressure conditions.

Concentrations of Ca²⁺ and Mg²⁺ increase throughout the course of the experiment (Figure 3a), as does the concentration of Mn²⁺, whereas Fe²⁺ (not shown) decreases due to precipitation and is not considered any further. The slopes of all three curves, however, decrease over time without reaching zero, thus indicating a continuous but diminishing dissolution of dolomite as is also obvious in the release rates calculated for Mg²⁺ and Ca²⁺ (Figure 3b). Both rates decrease by one order of magnitude. However, equilibrium is not reached. The Ca:Mg ratio decreases slightly from 1.4 to 1.2 during the first 27 hours (1800 min), i.e., 10 hours after heating. This change likely coincides with the dissolution of small calcite crystals incorporated in the dolomite (Figure 2). Thereafter, the Ca:Mg ratio of

1.2 is almost constant but elevated compared to the ratio of 1.0 in the solid, possibly caused by an incongruent dissolution behavior of dolomite.

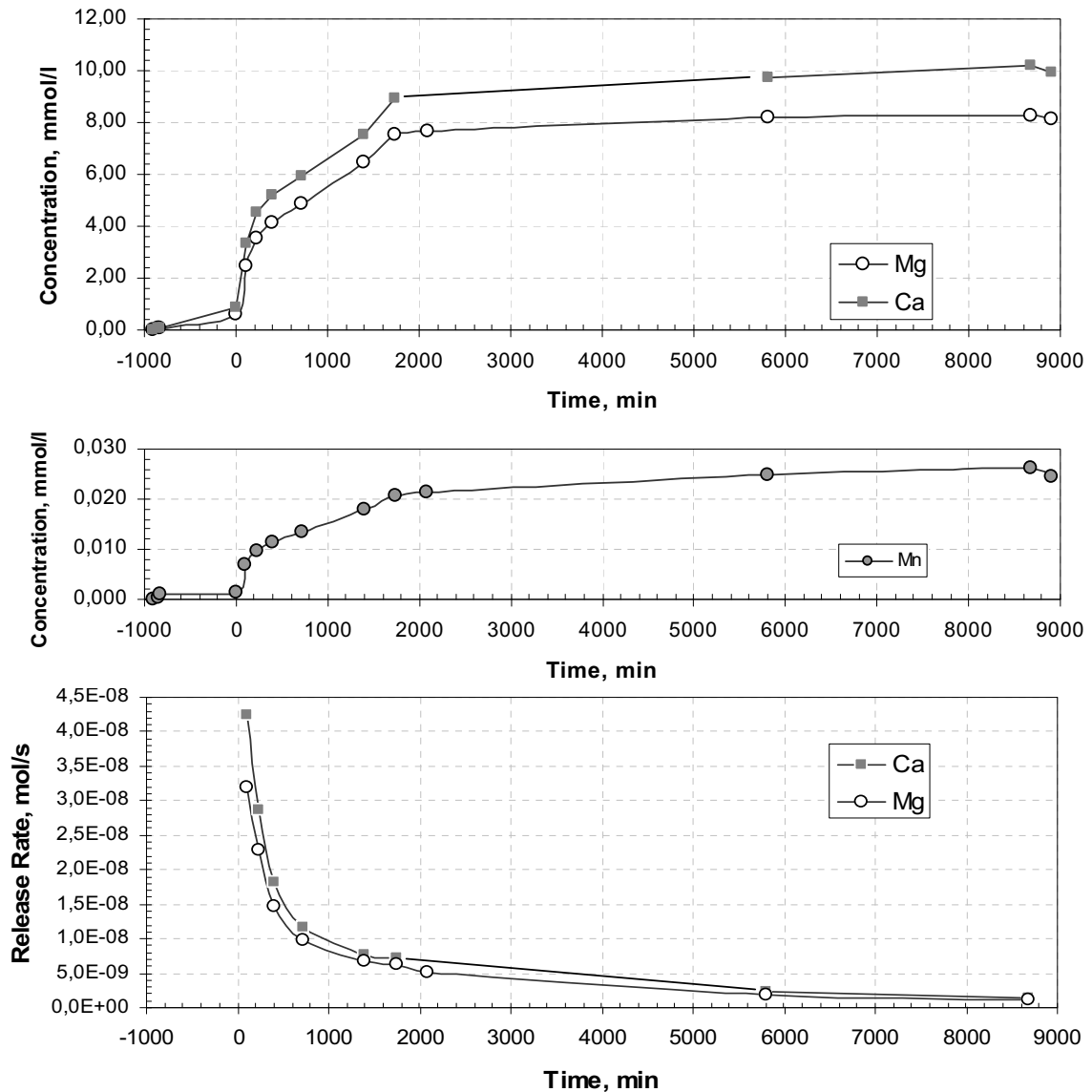


Figure 3 Temporal variations of aqueous Ca, Mg concentrations (mmol/l) (upper panel) and Mn concentrations (mmol/l) (central panel) in CO₂-saturated brine (150 g NaCl/l) during a batch-type HPHT experiment (120°C; 200 bar) using dolomite (CaMg(CO₃)₂) and a solid:liquid ratio of 1:20. The temperature was set to experimental conditions (120°C) 16 h after the pressure set to 200 bar, indicated by the start point. The last sample at 8900 min was taken after opening of the vessel. Errors associated with the analyses do not exceed ±3%. The CO₂ concentration was slightly below saturation since undissolved CO₂ was a major component of the first sample. The lower panel shows the release rates of Mg and Ca over the course of the experiment.

The final amount of dissolved Mn²⁺, Mg²⁺ and Ca²⁺ equals 1.8 – 2.8% of the amount of substances originally contained in the dolomite, suggesting that approximately 2% of the dolomite has been dissolved. This is true under the assumption that secondary minerals forming throughout the experiment did not include substantial amounts of

these cations. They do, however, include amounts of released and oxidized Fe^{2+} , as is obvious from the red color of the mineral surface after the experiment and a rough EDS analysis (Figure 4).

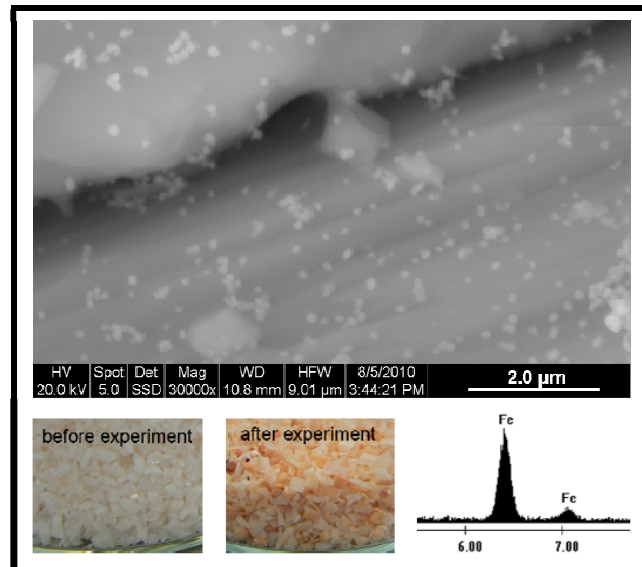


Figure 4 SEM image of the reaction product showing small roundish precipitates (upper panel) containing substantial amounts of Fe as pointed out by the clipping of a EDS image (qualitative analysis only) in the lower upper corner. This formation of iron precipitates on the minerals surface is also obvious in the visual comparison of the dolomite before and after the experiment (lower left corner).

4. Future Work

This first series of experiments using pure CO_2 serves as a measure for experiments using binary gas mixtures and simultaneously allows for the numerical simulations to be tested, adjusted and validated to the laboratory system. While dolomite and calcite have been investigated, a number of clay and feldspar minerals will follow now, taking into account gaps in database regarding pressure and temperature conditions. The focus of the following set of experiments will be on binary gas mixtures, such as $\text{CO}_2 + \text{O}_2$. At the same time the assemblage of the flow-through reactor system is taken forward as is the development of the method to measure isotope-labelled minerals on a small scale.

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