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Summary

This report describes preliminary long term modelling results of the expected geochemical impact of CO_2 injection in the Utsira Sand on the caprock at Sleipner based on the data available up to November 2002. It forms part of the SACS2 Addendum project (Saline Aquifer CO_2 Storage – extension TotalFinaElf), an extension of the European 5th Framework project ENK6-CT-1999-00014. This report reflects the contribution of BRGM to this project extension.

In the Sleipner area (Norwegian block 15/98), supercritical CO_2 is injected in the Pliocene Utsira Sand in which it migrates upwards. The Utsira Sand is overlain by sediments of the Nordland Group, which are reported to be mainly shales in their lower part. In principal these sediments will act as a seal for the Utsira Sands and inhibit vertical CO_2 migration. The goal of this modelling work is to assess the geochemical impact of the reactive diffusion of dissolved CO_2 into the caprock on the long term (at least 15000 years), to identify major mineral-water interactions and to assess their impact on the porosity of the caprock.

The modelling is based on the mineralogy of the caprock cuttings as described in Bøe and Zweigel (2001) and Kemp et al. (2001). Some conceptualisation of the mineral assemblage is necessary, as the description of the observed minerals is not specific enough to be defined as mineral phases in the model. A few different conceptual models for the mineral assemblage are considered. The initial composition of the caprock formation water is derived from equilibrium modelling based on the Utsira formation water since no direct measurements for the caprock formation water are available.

The code used for the modelling is the geochemical software package PHREEQC (V2.6) (Parkhurst and Appelo, 1999) and the modelling is built up in stages of increasing complexity:

- Equilibrium batch modelling of the caprock formation water saturated with CO_2 with the Nordland Shale sediment, with and without taking into account ion-exchange processes.
- Long term (15000 years) kinetic batch modelling of the CO_2-saturated caprock formation water with the Nordland Shale sediment.
- Long term (15000 years) diffusive transport modelling of CO_2 saturated caprock formation water into the caprock taking into account reaction kinetics.

The results of the equilibrium batch modelling, based on the conceptual models of mineral assemblage tested, suggest that the caprock will undergo mineralogical changes, of which the precipitation of chalcedony and kaolinite and the dissolution of illite are quantitatively the most important. Calcite dissolution is predicted but significant carbonate precipitation can occur as dolomite, magnesite, siderite or dawsonite, due to the release of carbonate forming elements (Mg, Fe, Na…) through the alteration of feldspars and clays. Depending on the caprock mineralogy, one can state that 1000 kg of

shale could theoretically trap between 30 and 66 kg CO_2. These mineralogical changes might affect hydraulic properties since porosity is expected to reduce significantly (18-24% theoretically). The impact of the ion exchange processes seems to be of minor importance in comparison to the dissolution and precipitation processes.

For the kinetic batch modelling, kinetic laws are based on the transition state theory and kinetic rates are selected from the literature. For the conceptual model of mineral assemblage tested, results show that over a 15000 years period two geochemical reactions, whereby CO_2 is sequestered, are dominating: the alteration of anorthite with the subsequent precipitation of kaolinite and calcite and the alteration of albite with the subsequent precipitation of chalcedony (quartz) and dawsonite. These reactions can reduce the porosity of the caprock by approximately 3% over the 15000 years period and a total amount of 14 kg CO_2 per 1000 kg caprock can be permanently sequestered.

However, large uncertainties in the mechanisms and parameters values are inherent to this type of kinetic simulations. These are situated at two different levels: the level of the mineral assemblage and the level of the description of the kinetic mechanisms. Because of these uncertainties, the timeframe in which these changes in porosity can occur has to be enlarged at least with one order of magnitude in each direction to 1500 - 150000 years after CO_2-injection. The uncertainty with respect to the mineral assemblage could be reduced if a more accurate description of the composition of the feldspars in the caprock would be available (ideally with a description of the composition of the solid solution). Reducing the uncertainty with respect to the kinetic mechanisms and parameters would require very long term experiments on the caprock under site specific circumstances and is therefore difficult to achieve.

The diffusion modelling shows that due to alteration of the feldspars, diffusion into the caprock is hindered. The rate at which the front representing highly dissolved CO_2 concentrations progresses into the caprock is calculated to be around 1.15 m per 1000 years, which is considerably lower than the calculated rate based on diffusion of CO_2 only without mineral interaction. This is based on the assumption that the plagioclase present in the caprock consists of a 50/50 mixture of albite and anorthite.

Due to the intensive alteration of the feldspars and precipitation of carbonates at the base of the caprock, the porosity can decrease by around 3%, further hindering diffusion to occur. The timeframe in which this decrease might occur is subject to the same level of uncertainty as the results from the kinetic batch calculations.

Four major conclusions can be drawn for this preliminary modelling with respect to the approach taken to model the long term impact of injection of CO_2 on the caprock. Although here specifically the conditions at Sleipner are modelled, certainly the first two conclusions will also apply to other (potential) CO_2-sequestration sites.

1. The modelling results clearly show that the impact on the porosity of the caprock due to geochemical interactions is very sensitive to two groups of parameters:

- the mineralogical composition of the caprock, including their availability to take part in geochemical interactions and the composition of solid solutions (here clearly illustrated for the plagioclase composition);

- the kinetics of crucial mineralogical interactions including their rates, pH–dependency, reactive surface area and the kinetic rate law itself.

2. Even for long term impact assessment the equilibrium approach is unlikely to be successful in predicting changes in porosity. When comparing the results from the equilibrium and the kinetic modelling after 15000 years (although minor differences in initial mineral composition are present) it becomes obvious that after 15000 years the system is still not at all in an equilibrium state and major mineral reactions modelled using the equilibrium assumption do not occur during the first 15000 years of the kinetic modelling.

3. This preliminary kinetic modelling suggests a reduction in porosity of the base of the caprock in the order of 3 % and a CO_2-sequestration capacity of 14.0 kg CO_2 per 1000 kg caprock over a 15000 years period.

4. The kinetic and diffusive transport approaches indicate that the impact of CO_2-injection on the caprock is limited in space. After 15000 years, only the base of the caprock (in this case the bottom 3 m section) will be affected by CO_2-rich formation waters.

At this stage, it is unclear how robust the obtained results are: very small changes in some parameter values (selection of primary or secondary minerals, reaction rates, etc.) can potentially lead to large variations in mineralogical reactions and porosity change. Estimating the robustness and the accuracy of the modelled results is crucial and requires detailed sensitivity analysis. Performing this analysis will be one of the challenges in the CO_2STORE project.

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1. Introduction

The physical and geochemical behaviour of the caprock when coming into contact with the supercritical CO_2 plume during and after injection is a key factor in the success of a CO_2 sequestration scheme. Due to its lower density, the CO_2 plume will rise in the reservoir rock. During this gravity segregation process the largely immiscible plume will displace the formation water and will partly dissolve (solubility trapping). Through this dissolution process interactions might occur with the reservoir rock itself (mineral trapping). Eventually the plume will reach the caprock and supercritical CO_2 will come into direct contact with the caprock and its formation water. The ability of the caprock to act as a seal and function as a structural trap for the plume will depend on the physical interactions between the CO_2 and the caprock (probably limited to diffusion only) as well as the geochemical interactions between the three end members, being the caprock mineralogy, the formation water of the caprock and the dissolving supercritical CO_2 phase. Geochemical reactions in the caprock can be both detrimental as well as beneficial with respect to its sealing capacity. Mineral dissolution could enhance porosity of the caprock and therefore its hydraulic conductivity, making the caprock more permeable. On the other hand, mineral precipitation could reduce the porosity of the caprock and increase mineral trapping of CO_2.

Identifying and quantifying the geochemical interactions between the dissolved CO_2 and the caprock is extremely complex taking into account the long timescales and the difficulties involved in obtaining in situ measurements. Modelling is an indispensable tool to increase our understanding of the geochemical evolution of the system.

In the Sleipner area (Norwegian block 15/98), CO_2 is injected in the Pliocene Utsira Sand in which it migrates upwards. The Utsira Sand is overlain by sediments of the Nordland Group, which are reported to be mainly shales in their lower part. These sediments are expected to provide a seal for the Utsira Sands and to inhibit vertical CO_2 migration. The geochemical aspects of the ability of the Nordland Shales to prevent upward movement of CO_2 are investigated in this report.

Earlier geochemical modelling, carried as part of the SACS2-project, assessed the interaction of high dissolved concentrations of CO_2 in the formation water with the minerals present in the Utsira sand through the interpretation of laboratory experiments (Czernichowski-Lauriol et al., 2002).

2. Conceptualisation and end-members

In order to model the geochemical interactions in the Nordland Shale, physical processes leading to interactions between the injected CO_2, the formation water and the sediment have to be identified. Also a conceptualisation of the geochemical processes is needed. This geochemical conceptualisation might start simple (e.g. batch modelling) but can gradually become very complex (e.g. involving kinetics and ion exchange calculations). In this process the results of each step of increasing complexity should be analysed carefully because of the large amount of uncertainty in processes and parameters involved in this type of modelling. The data for the geochemical interactions are defined by the end-members, which are in this case: the formation water in the caprock, the mineralogy of the caprock and the injected CO_2.

2.1. CONCEPTUALISATION OF THE INTERACTION WITH THE CAP-ROCK

When assessing the geochemical impact of CO_2 sequestration on the caprock, different mechanisms changing the pristine situation of the caprock have to be investigated. Different products of interactions between CO_2, formation waters of both the reservoir and the caprock and minerals of the reservoir will ultimately come into contact with the caprock itself.

The area where the impact on the caprock is expected to be the most intensive is the top of the injected CO_2-plume, where the caprock formation water, which will become saturated with CO_2, interacts with the caprock over an extensive area. It is this type of interaction that is studied in this report.

2.2. PHYSICAL PROCESSES

Although the presence of small quantities of smectite in the Nordland shale may invalidate its predictions, based on pore throat diameters, capillary entry pressures suggest no capillary leakage of CO_2 through the top of the seal takes place. This analysis is based on leakage through a pore network only and ignores possibly more effective pathways provided by the presence of microfractures (Kemp et al., 2001). This is also confirmed by Bøe and Zweigel (2001) who state that capillary leakage of CO_2 through the top seal is unlikely to occur. The main mechanism of transport of CO_2 through the caprock is therefore diffusion.

Diffusion into the caprock can be described by Fick's law for diffusion in sediments (Domenico & Schwartz, 1990):

$$J = -D_d^{'} \ grad(C) \tag{1}$$

with J: the diffusional flux (moles/L^2T); D'_d the effective diffusion coefficient (L^2/T) and C the concentration (moles/L^3).

The following equation links the D'_d for the fluid in a porous medium to the diffusion coefficient in a liquid D_d using the porosity n of the porous medium (based on Helfferich, 1966):

$$D'_d = \frac{n}{2} D_d \quad to \quad D_d \left[\frac{n}{(2-n)} \right]^2 \tag{2}$$

The diffusion coefficients for most ions and gasses at defined temperatures are available in the literature. Based on the porosity the effective diffusion coefficient can be estimated. Many empirical and theoretical methods for the calculation of the diffusion coefficient exist, which can take into account other parameters (e.g. tortuosity).

2.3. CHEMICAL PROCESSES

2.3.1. Reservoir characteristics

At Sleipner the reservoir is at 37°C and the hydrostatic pressure is 10 MPa. The maximum CO_2 pressure which can be reached according to this hydrostatic pressure is also 10 MPa, which corresponds to a CO_2 fugacity of 52 at 37°C according to the formula described in Duan et al. (1992). During the simulations this fugacity value of 52 is used. During injection, a significant pressure on top of the hydrostatic pressure can build up. This overpressure is not taken into account during the modelling.

2.3.2. Endmembers

The geochemical system consists of three endmembers: the injected CO_2, the caprock formation water (CFW) and the caprock mineralogy. Since the composition of the caprock formation water is derived from the Utsira formation water, the latter can also be seen as an endmember.

Nordland Shale Caprock

The Nordland Shale Caprock mineralogy is described by Bøe and Zweigel (2001) for the Nordland Shale in the Norwegian sector of the North Sea (Norwegian block 15/9) and by Kemp et al. (2001) for the Nordland Shale in the UK sector (Quadrant 14). A few clay mineralogy analysis from the Nordland Shale at Sleipner and its possible analogue from the Ekofisk area are described in Lindgren et al. (2002).

The cutting samples analysed by Bøe and Zweigel (2001) are from the Sleipner area close to the injection site. As a representative of the Nordland Shale, the data of 4 samples of the lower end of the Nordland Shale taken at 10 cm depth intervals are averaged (sample numbers 15/9-9.775, 15/9-9.785, 15/9-9.795 and 15/9-9.805) in order to average out local variabilities. The resulting composition is shown in Table 1. These samples are taken at a distance of up to several tens of meters above the top of the Utsira Sand.

The mineralogy of the mudrock samples taken from the Nordland Shale in UK Quadrant 16, northern North Sea (Kemp et al., 2001) is described in more detail. It is also shown in Table 1 and can be summarized as clay silts or silty clays with an average composition of quartz (30%), undifferenciated mica (30%), kaolinite (14 %), K-feldspar (5%), calcite (4%), smectite (4%), albite (2%), chlorite (1%), pyrite (1%) and gypsum (1%). The clay mineralogy is generally dominated by illite with minor kaolinite and traces of chlorite and smectite. The clay and silt fractions of the samples are dominated by clay minerals and detrital phyllosilicates while the small portions of fine sand grade material are predominantly composed of quartz and K-feldspar with some rare bioclastic debris. The samples have traces of organic carbon and have CEC values of 18 meq/100 g. All the samples are very poorly porous and contain limited volumes of microporosity which occurs between typically tightly packed clay particles. These micropores constitute only a few percent of the total rock volume, are circa 1 μm in diameter and are poorly connected to each other (Kemp et al., 2001).

All minerals fractions present in a percentage ≥ 1% (except for the low percentage of mixed layer clays in the Norwegian composition because the description is too unspecific) are included in the modelling and the amounts are recalculated to 100%. For the calculation of the amount of minerals available for reaction in 1 litre of caprock water a porosity of 5% and a bulk density of 2750 g/l for the caprock were assumed.

Some conceptualisation of the mineral assemblage is necessary. This because the description of the observed minerals is not specific enough to allow it to be defined as a mineral phase in the model. Chlorite is a description for a group of minerals, clinochlore, a member of the chlorite group, for which the thermodynamics is known, is selected. The phase described as undifferenciated mica in the case of the UK description and mica/illite in the case of the Norwegian description is modelled as illite. The phase described as smectite again allows a wide variation in mineralogical composition, a Mg and Fe rich variation was selected for the modelling. It is further assumed that the unspecified plagioclase in the case of the Norwegian Nordland Shale consists of albite only. This latest selection is also made to allow the model to converge and the plagioclase composition will be refined for the kinetic modelling in the next section. Finally, chalcedony was selected instead of quartz, which is normally the controlling SiO_2–phase in sedimentary rock at low temperatures.

The presence of pyrite in the assemblage has to be treated with caution since its behaviour is determined by the redox conditions of the system for which no information is available. To assess the stability of pyrite in the assemblage an estimate of the pe value is necessary since it is not measured.

Based on the two sediment descriptions it becomes obvious that the qualitative difference between both is relatively minor, but that quantitative differences are important.

Table 1 - Mineralogical composition (only fractions ≥1%) of the Nordland Shale at Sleipner according to Boe and Zweigel (2001) and Kemp et al. (2001) and their conceptualisation in the geochemical model .

Nordland Shale UK Quadrant 16				
Observed mineral	Mass per-cent (%)	Modelled mineral	Mass per-cent (%)	Moles in contact with 1l pore water
Albite	2	Albite	2	4.4
Calcite	4	Calcite	4	23.3
Quartz	30	Chalcedony	30	290.8
Chlorite	1	Clinochlore 7A	1	1.0
Gypsum	1	Gypsum	1	3.4
Smectite	4	High Fe-Mg Smectite	4	5.8
Undifferenciated mica	30	Illite	30	45.5
Kaolinite	14	Kaolinite	14	31.6
K-feldspar	5	K-feldspar	5	10.5
Pyrite	1	Pyrite	1	4.8
Total	**92**		**92**	
Nordland Shale Norwegian area				
Observed mineral	Mass per-cent (%)	Modelled mineral	Mass per-cent (%)	Moles in contact with 1l pore water
Plagioclase	12.3	Albite	12.3	26.6
Calcite	1.0	Calcite	1.0	5.6
Quartz	21.5	Chalcedony	21.5	196.0
Chlorite	4.1	Clinochlore 7A	4.1	4.0
Smectite	8.8	High Mg-Fe Smectite	8.8	11.9
Mica/Illite	24.7	Illite	24.7	35.2
Kaolinite	18	Kaolinite	18	38.1
K-feldspar	2.1	K-feldspar	2.1	4.1
Pyrite	2.8	Pyrite	2.8	12.9
Siderite	1.6	Siderite	1.6	8.6
Mixed layer Clay	1.4	Not modelled	0	0
Total	**98.3**		**96.9**	

Nordland Shale Formation water

No data exists on the interstitial water from the Nordland Shale since the only samples available are cuttings (Lindgren et al., 2002). In July 2002 the Nordland Shale was sampled at Sleipner as part of the SACS2 project, which should allow analysis of the pore water by the SACS2 partners. However, at the time this modelling is executed no data with regard to this analysis are available.

Over time, a mixing zone between Utsira formation water and Nordland Shale Formation water will have developed at the top of the Utsira Sands and the base of the Nordland Shale. One can therefore assume that the formation water at the base of the Nordland Shale has at least some component of the Utsira Sand formation water, which is in equilibrium with the Nordland Shale. Hence, as a surrogate for the Nordland Shale formation water the Utsira formation water is equilibrated with the mineralogy of the Nordland Shale.

Utsira Formation water

Also for the Utsira formation no direct data on the formation water composition are available. Samples are taken from core from the 15/9-A23 well but the analysis showed an important component of mixing with the drilling mud leading to non realistic potassium and chloride concentrations. This contamination made the use of the analysis for the modelling impossible.

A pore water sample analysis from the Oseberg field, which is located 200 km north of the Sleipner field, is the best surrogate for the formation water in the Utsira Sands. However the analysis is incomplete in that no Al and Si were measured. These parameters are essential for geochemical modelling. During the SACS-project BGS carried out batch experiments whereby a synthetically composed formation water was brought into contact with samples from the Utsira formation. The composition from the synthetically composed formation water was based on the analysis from the Oseberg sample (Rochelle and Moore, 2002).

The composition of this synthetic water in contact with the Utsira sand after three months was used as a starting point for the Utsira Formation water. Modelling of the experiments (Czernichowski-Lauriol et al., 2002) pointed out that the measured Al concentrations in these samples were problematic. However, to obtain the caprock formation water this water is equilibrated with the minerals present in the caprock, which causes important changes in its composition, thereby wiping out its initial signature.

The composition of the water was analysed after being in contact with the Utsira sediment for 3 months. This composition is assumed to show the largest similarities with the real Utsira formation water and is used during the geochemical modelling.

In Table 2 the composition of the Oseberg sample, the synthetic Utsira water and the resulting water composition from the batch experiment are shown.

Table 2 - Data availability on formation water regarding the Utsira sands (after Czernichowski-Lauriol et al., 1999)

	Oseberg pore water	**Synthetic Utsira pore water**	**Utsira batch water**
Parameter			
P (MPa)	7-9	10	10
T (°C)	23	37	37
pH	7.1	7.77	7.82
Elements (mg/l)			
Na	10392	10306	10528
K	208	225	239
Mg	630	633	629
Ca	426	432	376
Sr	10	10	9.29
Ba	0.5	0.31	3.70
Total Fe	2	1.21	9.07
Al	-	<2.0	1.94
Total S	-	1.05	16.9
Si	-	<DL	0.87
SiO2	-	<DL	1.86
Cl	18482	18659	18621
Br	-	< 2.00	< 6.00
SO4	ND	< 2.00	< 60.0
HCO3**	707	386	349

** Value might be underestimated

3. Numerical modelling

3.1. INTRODUCTION

The modelling is built up in stages of increasing complexity. During the different stages sensitivity analyses will be carried out. The purpose of the modelling is to identify:

- The geochemical processes or parameters to which the penetration of high CO_2 concentrations in the caprock is the most sensitive.
- The major mineralogical changes in the caprock as a consequence of CO_2 injection and its potential influence on physical properties such as porosity and permeability.
- The information gaps and needs for further investigations.

The different stages are:

- Generation of the caprock formation water
- Equilibrium batch modelling of the caprock formation water saturated with CO_2 with the Nordland Shale sediment
- Equilibrium batch modelling of the caprock formation water saturated with CO_2 with the Nordland Shale sediment taking into account ion-exchange processes
- Kinetic batch modelling of the caprock formation water with the Nordland Shale sediment
- Diffusion of CO_2 saturated caprock formation water into the caprock taking into account reaction kinetics

The code used for the modelling is the PHREEQC (V2.6) code (Parkhurst and Appelo, 1999), while the database used was the PHREEQC.dat database.

3.2. BATCH MODELLING

3.2.1. The caprock formation water (CFW)

To assess the compatibility of the Utsira formation water with the minerals present in the caprock, the saturation indices of these minerals are calculated under in situ conditions (Table 3; in italics also saturation indices for crucial carbonates are listed). The experimental Utsira batch water is not in equilibrium with the mineralogy present in the caprock. The same observation was made with respect to the mineralogy present in the Utsira Sand (Czernichowski-Lauriol et al., 2002). Only the minerals chalcedony and gypsum are undersaturated, all other minerals present in the caprock are supersaturated. The initial composition of the Utsira formation water will therefore undergo significant changes when equilibrated with the caprock minerals.

The experimental Utsira batch water is subsequently equilibrated with all the minerals present in the caprock to generate the caprock formation water (CFW). Two calculations are executed, one for the UK Nordland Shale description and one for the Norwegian Nordland Shale description.

Table 3 - Saturation indexes for the experimental Utsira batch water (T = 37°C; pH = 7.82; pe = -4.0; initial pCO_2).

Mineral	SI	Mineral	SI
Albite	1.12	Illite	5.2
Siderite	1.11	Kaolinite	4.43
Chalcedony	-0.93	K-Feldspar	2.11
Clinochlore 7A	6.68	Gypsum	-2.28
Quartz	-0.67	*Barite*	0.49
Smectite-high-Fe-Mg	3.87	*Dawsonite*	*-3.29*
Calcite	1.02	*Dolomite*	*3.68*

For this equilibrium calculation also saturation with respect to dolomite, dawsonite, barite and siderite is defined, which means that these minerals can precipitate only if supersaturation exists. The resulting water composition can only be seen as a surrogate for the actual CFW, but is a best estimate based on the limited data available. The composition of the CFW as it is used for further modelling is shown in Table 4.

3.2.2. Equilibrium batch modelling of CO_2 saturated formation water (CO_2-CFW) in contact with the caprock

Boundary conditions

The boundary conditions have to be chosen in such a way that the modelled geochemical reactions are in accordance with the reactions that will occur in situ in the caprock in reality. The major reactions expected to occur when CO_2 is added to the formation water of a sediment are:

- The alteration and formation of aluminosilicate minerals.
- The dissolution and precipitation of carbonate minerals (e.g. dolomite, calcite)

The boundary conditions have to be defined in such a way that these interactions can take place. For the equilibrium simulation it is therefore assumed that the CO_2-saturated caprock formation water could reach equilibrium with all the minerals present in the caprock (chalcedony, illite, kaolinite, K-feldspar, calcite, smectite, clinochlore, albite, gypsum and pyrite) and that also equilibrium with the main carbonate minerals can be reached (calcite, siderite, dawsonite, dolomite, magnesite). Pyrite is also considered in the selected set of minerals, however the stability of pyrite is very sensitive to the redox conditions of which no direct information is available.

At the end of the simulation all mineral indices are calculated based on the composition of the resulting formation water. When the solution is not heavily supersaturated towards minerals not included in the equilibrium assemblage, it is assumed that the selected minerals is acceptable.

Table 4 - Modelled composition of the caprock formation water (CFW (UK) and CFW(N) and the CO_2-saturated caprock formation water in equilibrium with the caprock based on the UK Nordland Shale (CO_2-CFW(UK)) and on the Norwegian Nordland Shale (CO_2-CFW(N)).

	CFW (UK)	CFW (N)	CO_2-CFW (UK)	CO_2-CFW (N)
Temperature (°C)	37	37	37	37
Ionic Strength	0.719	0.647	0.677	2.034
pH	7.62	7.67	4.65	4.31
pe	-3.84	-4.07	-0.47	0.43
imposed f_{CO2} *	-	-	52	52
Elements (moles/kg H_2O)				
Al	3.14E-08	3.51E-08	5.53E-07	3.94E-06
Ba	9.87E-07	1.25E-05	9.87E-07	3.36E-08
C	5.10E-05	6.92E-05	1.76E+00	9.44E-01
Ca	2.01E-01	1.77E-01	1.38E-01	1.24E-02
Cl	5.29E-01	4.79E-01	5.29E-01	2.18E+00
Fe	3.03E-07	2.48E-07	6.74E-03	1.33E-02
K	1.61E-04	1.42E-04	1.50E-01	2.56E-01
Mg	1.30E-02	1.11E-02	8.61E-03	1.45E+00
Na	1.17E-01	1.06E-01	1.39E-01	2.67E-01
S	6.37E-03	4.81E-04	5.62E-05	5.97E-01
Si	2.48E-04	2.52E-04	2.42E-04	1.77E-04
Sr	1.07E-04	9.66E-05	1.07E-04	4.40E-04
H_2O Mass (kg)	1.00	1.11	1.00	0.22**
Saturation indices				
Albite	0	0	-2.90	-2.89
Calcite	0	0	0	-1.56
Chalcedony	0	0	0	0
Clinochlore 7A	-0.15	0	-31.07	-23.33
Dawsonite	-3.26	-3.29	0	0
Dolomite	0	0	0	0
Gypsum	0	-1.15	-2.22	0
Illite	0	0	-1.54	-1.14
Kaolinite	0	0	0	0
K-feldspar	0	-0.01	0	0
Magnesite	-1.56	-1.56	-1.56	0
Siderite	-3.77	-3.8	0	0
Smectite-high-Fe-Mg	0	0	-9.16	-7.30

* imposed f_{CO2} according to a pCO_2 of 100 atm.

** the reduction the mass of H_20 present is a consequence of the alteration of large amounts of albite as discussed in the text.

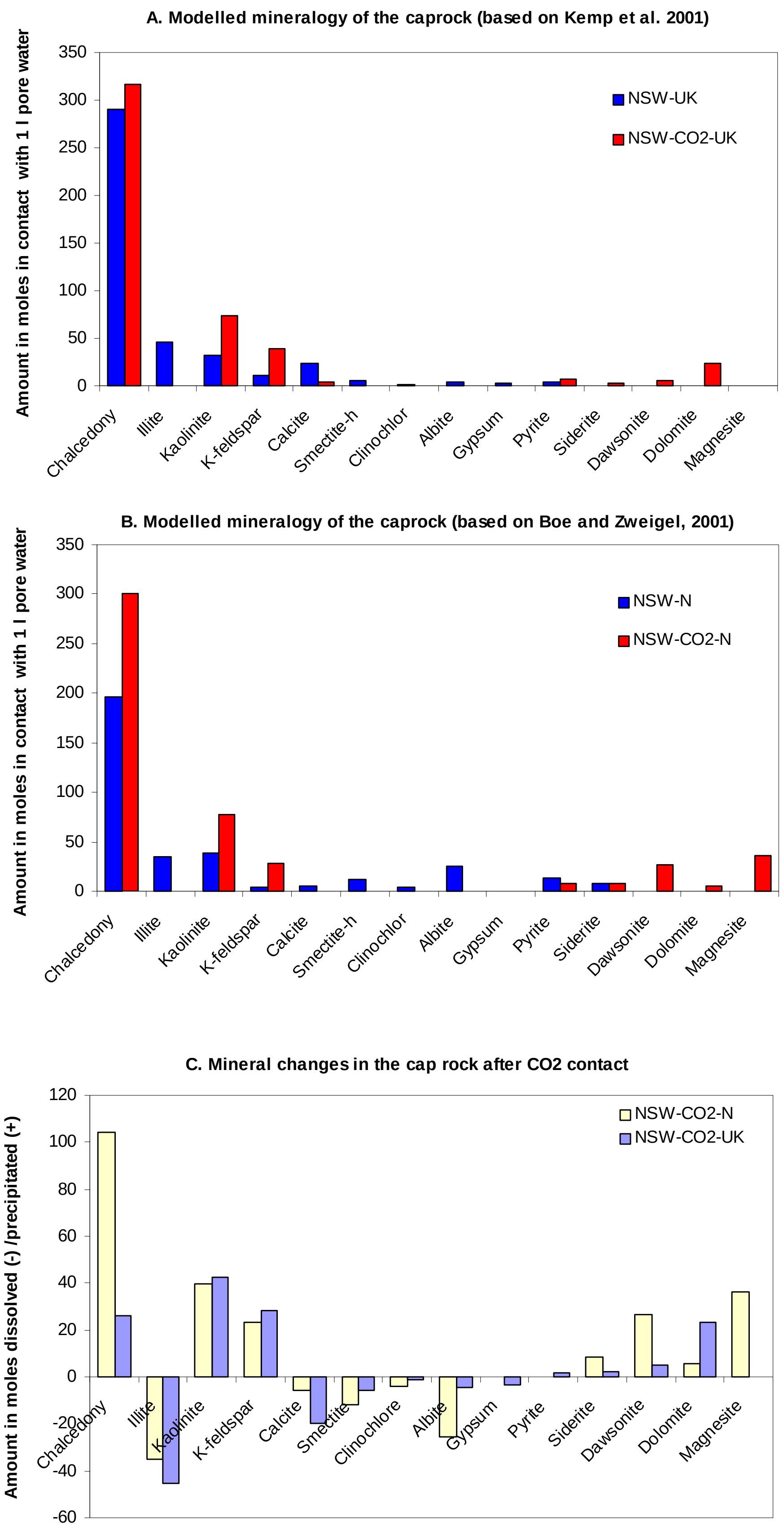

Figure 1 - Mineralogical changes in the caprock due to the dissolution of CO_2 in the caprock formation water under equilibrium conditions (37°C, pCO_2=10 MPa).

Results

As stated above, equilibrium with a large number of minerals is imposed. This is unlikely to represent reality and the results from the equilibrium modelling under CO_2 saturated conditions should therefore be seen as a “highest impact” case or an opposite to the case where no interaction with the caprock occurs. The quantitative mineral changes are shown in Figure 1 and listed in Table 5.

Table 5 - Mineralogical changes in moles per kg H_2O when CO_2-saturated) caprock water (at 37°C and pCO_2 = 10 MPa) assuming equilibrium with minerals present in the caprock.

	Caprock mineralogy Bøe & Zweigel (2001)	Caprock mineralogy Kemp et al. (2001)
Chalcedony	104.18	25.87
Illite	-35.21	-45.51
Kaolinite	39.6	42.50
K-feldspar	23.5	28.3
Calcite	-5.61	-19.62
Smectite-high Mg-Fe	-11.93	-5.76
Clinochlor	-3.99	-1.04
Albite	-25.59	-4.44
Gypsum	0.21	-3.38
Pyrite	-0.17	1.69
Siderite	8.52	2.33
Dawsonite	26.83	4.99
Dolomite	5.87	23.21
Magnesite	36.30	0.00

Limits of using PHREEQC with respect to equilibrium modelling

In the case of the Norwegian Nordland Shale, the equilibrium assumption pushes PHREEQC over its limits of applicability. Indeed, PHREEQC uses an ion-association model (based on Debye-Hückel or Davies approach) to calculate thermodynamic properties and, according to the authors, this model starts to break down at higher ionic strengths, somewhere between .7 and 2 molal, depending on solution composition. This means that any calculation that involves large amounts of complexing at high ionic strength (>0.7) is questionable. The equilibrium modelling leads to highly mineralised waters with a ionic strength of 2.034 molal. This is far beyond the applicability limits and therefore the results have to be treated with caution. The calculated amounts of dissolved and precipitated minerals might therefore have a low reliability.

To avoid this problem with highly mineralised solutions, one could consider using a model based on the Pitzer formalism. However, this approach has as a drawback that Al speciation cannot be calculated since parameter values for Al are currently not known. Here, Al is crucial for the equilibrium calculation with respect to aluminosilicate minerals.

Mineralogical changes in the caprock

The results from the equilibrium interaction with both caprock mineralogies show the same overall dissolution and precipitation pattern when in contact with a large amount of dissolved CO_2. Chalcedony, kaolinite and K-feldspar precipitate at the expense of illite, calcite, smectite and albite. Significant carbonate precipitation occurs as siderite, dawsonite, dolomite and also magnesite in the case of the Norwegian composition. In both cases significant alterations in the silicate minerals induce the precipitation of the carbonates. The dissolution of calcite and the recristallisation as dolomite is likely to be linked to the excess of Mg coming into solution due to the smectite alteration .

A total of 77.9 mole CO_2 per kg water in contact with the sediment is sequestered in the mineral phase in the case of the Norwegian caprock mineralogy. For the UK caprock mineralogy this reduces to 35.9 moles CO_2 per kg water. Mineral trapping is the main mechanism for sequestration. The mineral composition described by Bøe and Zweigel (2001) is much more reactive that the one described by Kemp et al. (2001). This is possibly linked to the high modelled albite content (assumed to represent plagioclase in the mineral description) leading to excess Na in the solution and therefore favouring the formation of dawsonite.

Pyrite precipitates slightly in both cases, its behaviour is highly dependent on the redox condition, for which no data are available, and therefore results should be interpreted with caution.

CO_2-CFW composition

The resulting CO_2-CFW composition, both based on the UK mineralogy and the Norwegian mineralogy is listed in Table 4.

The pH, which decreases significantly when the caprock formation water is brought under CO_2-pressure only, becomes buffered when the water interacts with the sediment to 4.65 in the case of the UK caprock mineralogy and 4.31 in the case of the Norwegian caprock mineralogy.

Due to the high concentration of dissolved CO_2 and the interaction with the minerals the bicarbonate concentration increases. The large amount of dissolved illite leads to potassium dominated waters in the case of the UK-caprock mineralogy. In the Norwegian caprock mineralogy the dissolution of more Mg-rich smectites leads to Mg cation dominated waters. In the case of the UK caprock mineralogy the precipitation of the carbonates reduces the Ca concentration in the solution and is likely to trigger the dissolution of the gypsum initially present.

In the case of the Norwegian caprock mineralogy a large amount of the water present is consumed during the important mineralogical transformations such as dissolution of albite (25.6 moles) with the subsequent formation of quartz and dawsonite. Initially 1l water or 55.6 moles of H_2O are present. This amount reduces to 0.22 l or 12.2 moles at the end of the simulation. This effect causes a concentration of the solution by a factor of 5 whereby the concentration of ions such as chloride, which does not take part in any reaction, increases.

Porosity and permeability changes

The change in volume of the total mineral assemblage before and after contact with the CO_2 can be used as an estimate for the change in porosity due to the dissolution and precipitation of the minerals. When this change is recalculated taking into account the initial porosity and subsequently subtracted from the initial porosity (in the case of increasing mineral volume) or added (in the case of decreasing mineral volume) to the initial porosity, the change in porosity can be calculated. For the Nordland Shale it is estimated that the initial porosity is 5 %. Contact with CO_2 causes the volume of the mineral assemblage to increase with 18 % in the case of the UK mineral assemblage and 24% in the case of the Norwegian mineral assemblage. For both compositions this means that porosity of the caprock completely disappears because the newly formed minerals fill all the pores initially present. However, these numbers are based on chemical calculations only and do not take into account physical reality.

Conclusions

The equilibrium batch modelling leads to the following conclusions:

- A significant amount of dissolved CO_2 reacts with the caprock formation water and the caprock mineralogy. Depending on the caprock mineralogy an amount between 36.0 and 78.0 moles of CO_2 will react with 1 kg formation water in contact with the sediment. Based on a porosity of 5% and an assumed shale density of 2750 kg/m^3, one can therefore state that 1000 kg of shale can trap between 30 and 65.7 kg CO_2 when all the shale comes into contact with the water. This is however unlikely to be the case and the calculated amounts indicate an upper limit.

- The pH of the formation water is likely to decrease, but is buffered by the alteration of aluminosilicate minerals.

- The caprock will undergo mineralogical changes, of which the precipitation of quartz (or chalcedony) and kaolinite and the dissolution of illite is quantitatively the most important next to the precipitation of carbonate minerals. These mineralogical changes might affect its hydraulic properties since porosity is expected to reduce significantly.

- Under the equilibrium assumption and according to the selected set of minerals within the conceptual geochemical model, the CO_2 saturated formation water in contact with the Norwegian Nordland shale becomes highly mineralised and the molar concentration of certain ions exceeds the limit above which PHREEQC computation becomes non-valid, rendering the calculated precipitated and dissolved amounts less reliable. However, the necessity to model the impact of clay minerals, requiring Al-speciation, does not allow Pitzer-based models to be used in this case.

In the absence of more accurate modelling, the results of the equilibrium modelling can be interpreted as a highest impact scenario.

3.2.3. Impact of cation exchange reactions

The high percentage of clays in the caprock might induce ion exchange processes. During ion exchange processes the initial cations or protons which are absorbed to the clays are exchanged for cations or protons in the formation water when its composition is no longer in equilibrium with the sediment.

This can influence the ongoing equilibrium reactions and therefore the precipitated and dissolved mineral amounts. The impact of ion exchange is therefore investigated based on the presence of two types of exchange sites.

Description of the cation exchange model

The ion-exchange model used for the modelling assumes that the thermodynamic activity of an exchange species is equal to its equivalent fraction multiplied by a Debye-Hückel activity coefficient. As stated by Appelo and Parkhurst (1999) site specific studies generally requires experimental data from the study site for appropriate model application. These data are not available for this study.

For the assessment of the impact of ion exchange processes, it is assumed that only two types of clays participated in the ion-exchange process: smectite and illite. An ion exchange capacity of respectively 100 and 25 meq/100 g is used. The exchange coefficients are taken from Gaucher et al. (2000) and listed in Table 6.

Table 6 - Ion exchange parameters (estimated at 25°C, here used at 37°C) used for the exhangers smectite and illite (Gaucher et al., 2000).

Parameter	Smectite	Illite
Log K H/Na	3.13	1.54
Log K K/Na	1.27	0.19
Log K NH_4/Na	1.004	0.310
Log K Ca/Na	0.795	0.795
Log K Mg/Na	0.624	0.624

The assemblage of the cations absorbed on the sites initially, before CO_2 injection, is obtained based on the assumption that equilibrium exists with the caprock formation water. The impact is only tested on the Norwegian mineral description.

Illite and smectite that precipitate during the modelling run also participates in the ion exchange process. The initially absorbed ion is K^+ in the case of illite and Mg^{2+} in the case of smectite for these newly formed mineral fraction.

Results and conclusions

In Figure 2 the impact of ion exchange processes on the mineralogical changes are illustrated. Modelling conditions were identical to the previous runs (37°C, pCO_2= 10 MPa).

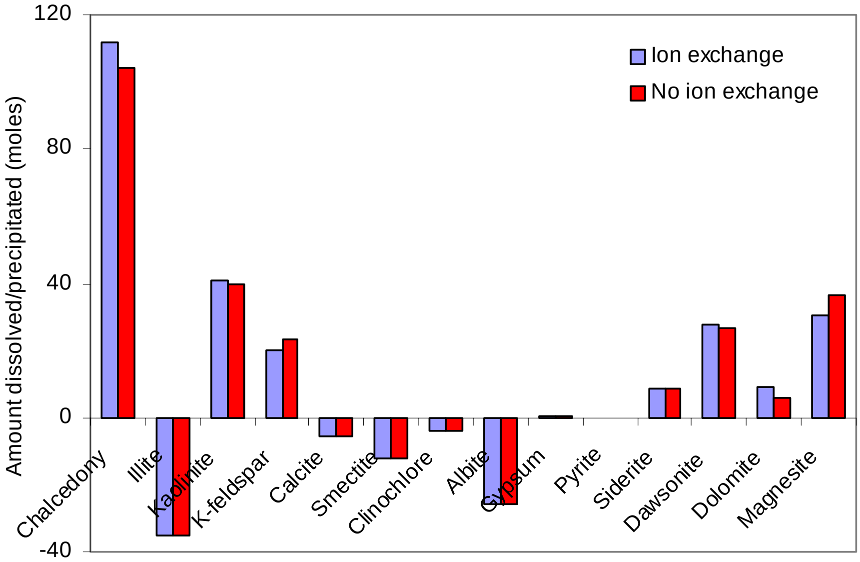

Figure 2 - Influence of ion exchange processes on the mineralogical changes in the caprock resulting from CO_2-injection.

The impact of the ion exchange processes is relatively minor and the error involved when ignoring ion exchange processes is small compared to the impact of other uncertainties in the mineral composition. It is therefore concluded that ion exchange is a process with little importance when assuming equilibrium conditions during CO_2 injection.

3.2.4. Kinetic batch modelling of CO_2 saturated formation water (CO_2-CFW) in contact with the caprock

The modelling of the kinetic aspects of geochemical interactions is indispensable when assessing the impact of CO_2 on the caprock. Mineral reactions are so slow that for some reactions even after hundreds of thousands of years equilibrium is not reached.

Therefore calculating the amount of CO_2 that can be trapped geochemically, based on the equilibrium assumption only, is likely to overestimate the actual amount after a distinct period of time. Modelling the dissolution and precipitation kinetics of complex systems does still involve many uncertainties. Both the rate constants as well as the dissolution and precipitation mechanisms are insufficiently known. Results from laboratory experiments only apply to specific circumstances which often different form the site specific circumstances to which the model should apply. The accuracy of the kinetic modelling results are therefore generally expressed in orders of magnitude.

Description of the kinetic model

The rate law for the kinetic mineral dissolution and precipitation used in the modelling is simplified from Lasaga (1994):

$$rate_m = A_m k(T)_m \left(a_{H+} \right)^n \left[1 - \left(\frac{Q_m}{K_m} \right) \right] \qquad (3)$$

where m is the mineral index, *rate* is the dissolution/precipitation rate (positive values indicate dissolution, negative values precipitation), A is the specific reactive surface per kg water, *k(T)* is the temperature dependent rate constant, a_{H+} is the proton activity, n is the order of the reaction ($0<n<1$), K is the equilibrium constant for the mineral water reaction written for the destruction of one mole of mineral and Q is the ion activity product.

The dependency of the rate constant on the temperature is defined as:

$$k(T) = k_{25} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \qquad (4)$$

where E_a is the activation energy (in J/mol), k_{25} is the rate constant at 25°C (in mol/m^2s), R is the gas constant (8.31 J /mol K) and T is the absolute gas temperature.

This rate law is applied to all the minerals present in the Norwegian Nordland Shale mineralogy apart from pyrite, for which a rate law based on Wiersma and Rimstidt (1984) is used:

$$rate = k(T) \frac{A \left(Fe^{3+} \right)}{m_{solution}} \qquad (5)$$

with $m_{solution}$ the mass of the solution in kg. This law reflects the redox determined behaviour of pyrite.

For all minerals it is assumed that the precipitation rate equals the dissolution rate.

Mineralogy

For the kinetic runs only the mineralogy described by Bøe and Zweigel (2001) is used (Table 1). Minor modifications are made to the mineralogical composition of the caprock (for the kinetic modelling only the Norwegian description will be used) compared to the equilibrium simulations. Dolomite is replaced by disordered dolomite since it is unlikely that the dolomite that precipitates as a consequence of CO_2-injection will form nicely shaped crystals. The plagioclase, which has been described as albite only so far, is now modelled as a mixture of albite and anorthite, being the two plagioclase end-members. Also during the kinetic modelling the CO_2 pressure is held constant.

Parameter selection

The kinetic rate parameters for the selected minerals are taken from the literature as indicated in Table 7. Where the rate parameter in the literature is listed for a different temperature, the value is recalculated for 37°C. Very little, inconsistent information exists in the literature on the value of the power (n) for individual minerals. Therefore a uniform average value for n of 0.5 is selected for all minerals.

The reactive surface area is a parameter which is extremely difficult to measure or calculate for in situ conditions. This results into an increased uncertainty of the modelled results of up to several orders of magnitude. Since no direct measurements of BET-surfaces are available for the Sleipner area, the geometric surface area is used for the calculation of the specific reactive surface area. The geometric surface area can be around 1 order of magnitude smaller than the BET-surface area due to the fact that the BET-surface area is also assumed to take into account surface roughness.

Interaction with the minerals is generally expected to occur only at selective sites at the surface and the difference between total surface area and reactive surface area can be between 1 and 3 orders of magnitude. Here, a scaling factor of 0.001 is used for all minerals to account for the difference between geometric surface area and the specific reactive surface area.

The geometric surface area is calculated assuming that mineral grains are spherical. For all the minerals, apart from the clays, an average grain diameter of 0.0033 m is assumed. This is the average diameter for the silt fraction, since these minerals make up the silt fraction in the sediment. Because also a minor sand fraction is present (Kemp et al., 2001), this grain diameter is likely to be a slight underestimation. For the clays an average grain diameter of 0.0002 m is taken which is the coarsest clay size. This is justified by the fact that also the silt fraction contains some “clay” minerals (Kemp et al., 2001).

The surface area for precipitating minerals is very difficult to estimate. Here it is assumed that for each mineral the reactive surface area during precipitation is 1000 times larger than the one for dissolution.

Results

Reduction of the calculation time

The length of the simulation based on the described parameter values is in the order of weeks when using a reasonable fast processor. These long calculation times are a known limitation with respect to long term geochemical simulations. To reduce the calculation time, the kinetics for kaolinite is eliminated and a saturation index of 1.43 with respect to kaolinite is defined at all times. This simplification will not affect the calculated results, except for the first timesteps. Shorter term simulation including the kinetics for kaolinite indicate that the saturation index of kaolinite stabilises very quickly at 1.43 and remains constant. The high concentrations of Si and Al coming into solution due to the dissolution of feldspars during the whole length of the simulation justifies this simplification. The fixing of the saturation index of kaolinite at 1.43 induces a dissolution rate for kaolinite according to a log *k* value of -9.6 which is at the higher end of experimental dissolution rates for kaolinite (Nagy, 1995), but is probably acceptable. This simplification with respect to kaolinite reduces the total calculation time by a factor of 100.

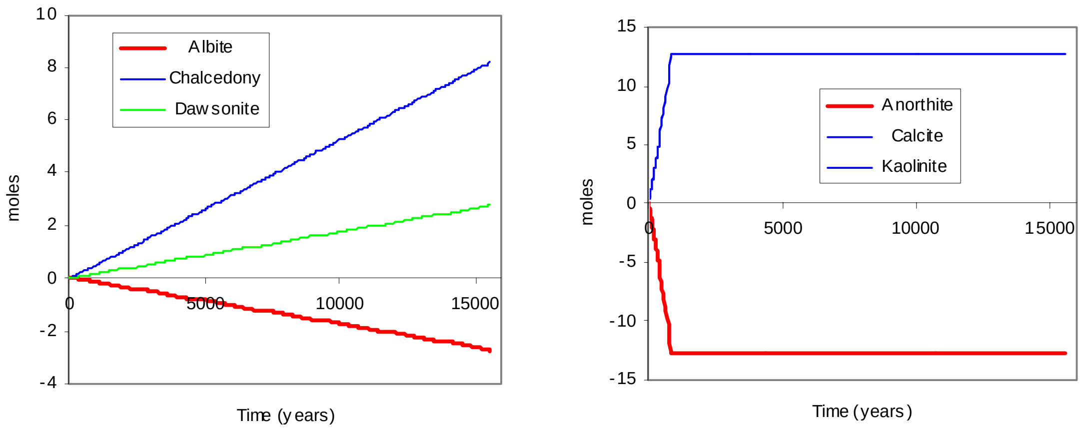

Figure 3 - Alteration of anorthite (right) and albite (left) versus time as a result of CO_2 injection.

Dominant geochemical reactions

The high concentration of dissolved CO_2 in the formation water induces alteration of the feldspars.

Both reactions lead to CO_2 sequestration (Figure 3):

1. The alteration of anorthite with the formation of kaolinite and calcite whereby CO_2 is sequestered as calcite:

$$CaAl_2(SiO_4)_2 + CO_2 + 2H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 \qquad (6)$$

2. The alteration of albite with the formation of chalcedony (quartz) and dawsonite whereby CO_2 is sequestered as dawsonite:

$$NaAlSi_3O_8 + CO_2 + H_2O \rightarrow 3SiO_2 + NaAl\ CO_3(OH)_2 \qquad (7)$$

The dissolution of anorthite occurs faster than the dissolution of albite and after 831 years most of the anorthite is dissolved. The alteration of feldspars has been reported in natural analogues by Watson et al. (2002) while high levels of dawsonite are described in a natural analogue by Baker et al. (1995). This mechanism therefore seems plausible.

The results suggests that other mineral interactions are of very minor importance or no importance.

The pH of the formation water stabilises around 4.3. Due to the consumption of H_2O in both reactions the solution becomes more concentrated whereby ions which do not take part in any reaction such as Cl and SO_4 increase as a consequence of that.

Total amount of CO_2 sequestered

The cumulated total amount of CO_2 sequestered in the liquid phase and in the mineral phase is shown in Figure 4. Solubility trapping consists of the amount of CO_2 dissolved in the water and the amount of CO_2 trapped as HCO_3^- and various other carbonate complexes ($NaHCO_3$, $CaHCO_3^+$, $NaHCO_3^+$, …). Solubility trapping occurs quickly with respect to the 15000 year timescale. Mineral trapping is the amount of CO_2 sequestered as calcite and dawsonite and depends on the rate of formation of these minerals. Where initially solubility trapping is the main mechanism for CO_2 sequestration, on the longer term, mineral trapping becomes more important and has an impact at the end of the simulation which is an order of magnitude larger than solubility trapping with a total cumulative trapped amount of 15.5 moles/l formation water.

The total amount of CO_2 trapped after 15 000 years in the caprock (which comes in contact with 1 l formation water) is 16.6 moles. This is 14.0 kg CO_2 per 1000 kg caprock (based on an estimated shale porosity of 5%, a density of 2750 kg/m^3 and a formation water density of 1 kg/l).

Influence on porosity

For each timestep the change in volume of the mineral assemblage is calculated based on the molar volumes of the dissolving and precipitating minerals. This change can be used as a measure for the change in porosity of that part of the caprock that comes into contact with CO_2 saturated formation water. Since the volume of the precipitating minerals is larger than the volume of the dissolving minerals a decrease in porosity is obtained. In Figure 5 the porosity evolution is shown based on an initial shale porosity of 5%. A total decrease in porosity of slightly over 3% is calculated, predominantly caused by the alteration of anorthite into calcite and kaolinite.

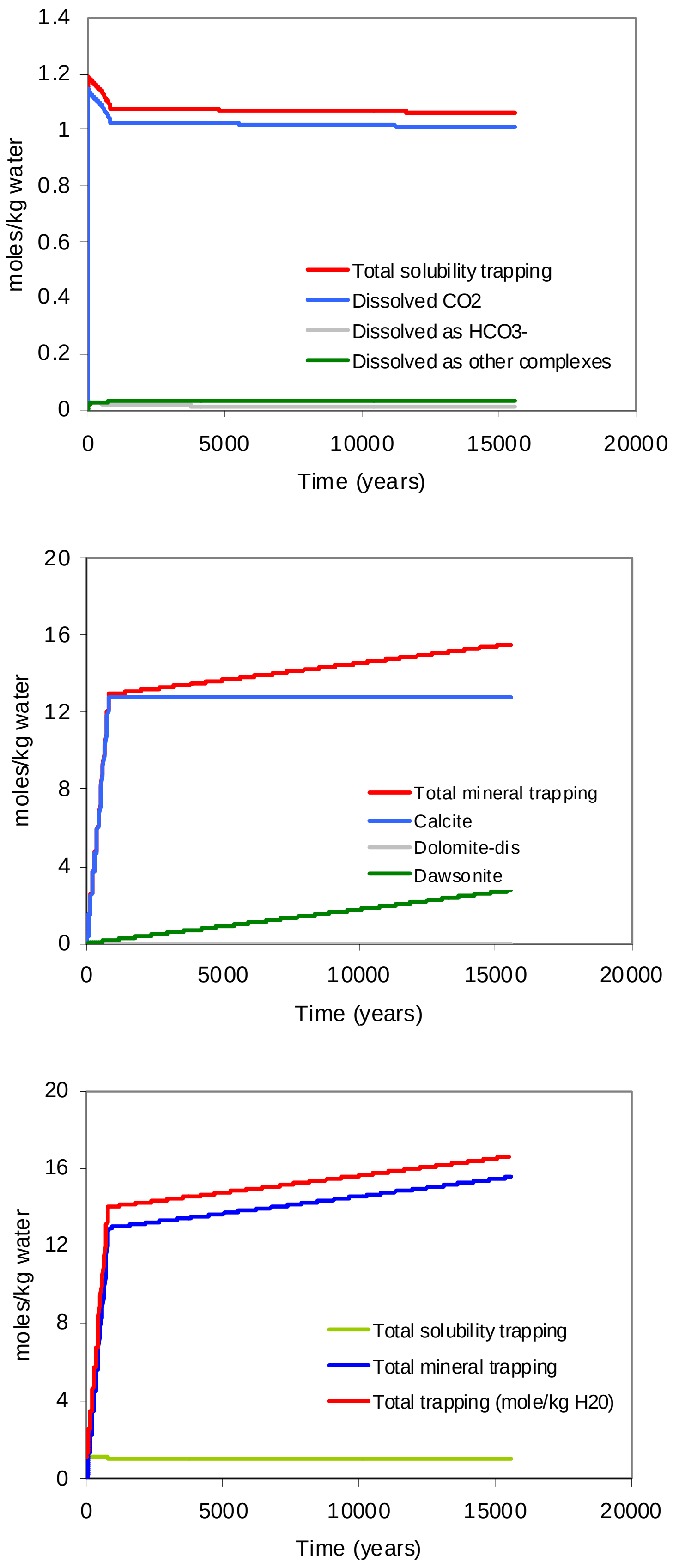

Figure 4 - Solubility trapping (upper), mineral trapping (middle) and total CO_2 trapping (lower) during the kinetic batch simulation.

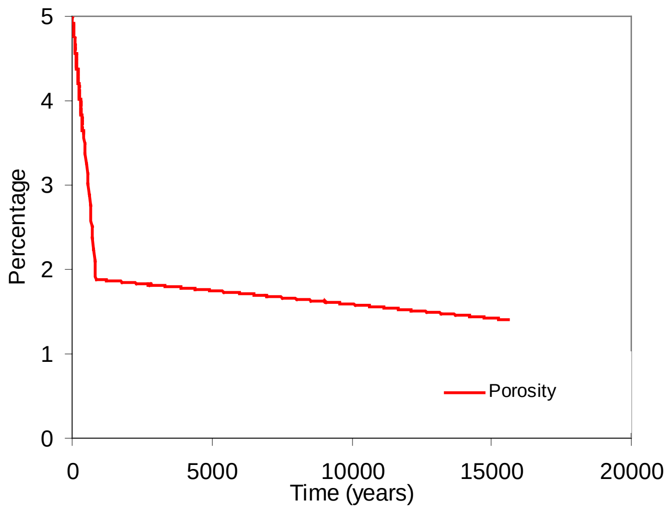

Figure 5 - Evolution of the porosity of the caprock where it is in contact with CO_2-saturated formation water due to mineralogical interactions (assuming an initial porosity of 5%) for a period of 15000 years.

Accuracy of the results

Uncertainty with respect to the mineral assemblage

The lack of information on the feldspar composition introduces a large uncertainty in the modelled results. The assumption stating that the amount described as plagioclase consists half of albite, half of anorthite has major implications on the results. Indeed, the much faster rate at which anorthite dissolves compared to albite leads to a quick depletion of anorthite. If the plagioclase present in the caprock would exist only of albite or an albite-anorthite solid solution, the amount of CO_2 sequestered and the porosity reduction can be significantly different.

Sensitivity of the precipitation rate of dawsonite

Data with respect to the kinetics of dawsonite are currently non-existing. Since dawsonite is a carbonate mineral it is reasonable that its precipitation and dissolution rate is of the same order as that for other carbonates. In the base case the rate of dawsonite is set intermediate to that of calcite and dolomite. In two subsequent runs the rate for dawsonite precipitation is set equal to that of calcite and that of dolomite, with *k*-values being $10^{-6.35}$ and $10^{-7.38}$ mol/m^2s respectively. The results from these simulations based on different rates for the precipitation of dawsonite after 10 000 years are identical (not shown). This illustrates that the modelled results are not dependent on the chosen rate constant for dawsonite kinetics within the range of carbonate dissolution and precipitation rates because the rates are sufficiently high to be considered as equilibrium precipitation.

Sensitivity of the reaction rates

The description of the kinetic rate mechanisms and the estimated parameter values is the component of the modelling of which the least is known. The uncertainty with respect to the rates is threefold and is present in the factor of the estimated reactive surface area of the minerals (based on the geometric surface area), the pH dependence of the reaction rates (*n* estimated to be 0.5) and the kinetic rate constant, taken from the literature. For the case studied here, the parameters with respect to the dissolving minerals (albite and anorthite) are the most critical. The most optimistic estimate of the accuracy would be one order of magnitude with respect to the overall rate at which anorthite and albite dissolve. This means that the total porosity change and the amount of CO_2 sequestered, here calculated after 15000 years, is expected to occur between 1500 and 150000 years after CO_2 injection.

Conclusions

The following conclusions can be drawn from the kinetic batch modelling.

- Based on the mineral assemblage as described from the cuttings in Bøe and Zweigel (2001) significant interaction between the CO_2 saturated formation water and the caprock minerals can occur. The processes dominating this interaction are the alteration of anorthite with the subsequent precipitation of kaolinite and calcite and the alteration of albite with the subsequent precipitation of chalcedony (quartz) and dawsonite.

- As part of these reactions 14.0 kg CO_2 per 1000 kg caprock is permanently sequestered in both carbonate minerals and in the formation water and the porosity is expected to reduce around 3% within the timeframe of interest, being 15000 years after injection. This porosity change is based on changes in molar volumes of dissolving and precipitating minerals only.

- Large uncertainties in the mechanisms and parameters values are inherent to this type of simulations. These are situated at two different levels: the level of the mineral assemblage and the level of the description of the kinetic mechanisms. Because of these uncertainties, the timeframe in which these changes in porosity can occur has to be enlarged at least with one order of magnitude each direction and becomes therefore between 1500 and 150000 years after CO_2-injection.

- The uncertainty with respect to the mineral assemblage could be reduced if a more accurate description of the composition of the feldspars and clays minerals in the caprock would become available (ideally with a description of the solid solution). Reducing the uncertainty with respect to the kinetic mechanisms and parameters would require very long term experiments on the caprock under the specific circumstances and is therefore difficult to tackle.

Table 7 - Mineral characteristics for the Nordland Shale used for the kinetic modelling

	Grain diameter (m)	Specific surface area (cm^2/g)	Total surface area ($m^2/kg\ H_2O$)	log(k(37°C)) (mol $m^{-2}\ s^{-1}$)	Source
Albite	3.30E-03	6.95E+02	2.33E+02	-8.44	Blum and Stillings (1995)
Anorthite	3.30E-03	6.59E+02	2.34E+02	-6.44	2 orders of magnitude higher than Albite as suggested in Blum and Stillings (1995)
Calcite	3.30E-03	6.71E+02	3.77E+01	-6.35	Azaroual et al. (2002)
Chalcedony (Quartz)	3.30E-03	6.86E+02	8.09E+02	-11.73	Azaroual et al. (2002)
Clinochlore-7A	2.00E-04	1.13E+03	2.51E+02	-11.63	Nagy (1995)
Dawsonite	3.30E-03	8.49E+02	1.08E+01	-6.86	Intermediate between calcite and dolomite
Dolomite	3.30E-03	6.35E+02	1.17E+01	-7.38	Azaroual et al. (2002)
Gypsum	3.30E-03	7.89E+02	1.36E+01	-7.38	Azaroual et al. (2002)
Illite	2.00E-04	4.68E+03	6.33E+03	-13.08	Nagy (1995)
Kaolinite	2.00E-04	1.16E+04	1.14E+04	-12.54	Nagy (1995)
K-feldspar	3.30E-03	7.11E+02	8.08E+01	-8.79	Blum and Stillings (1995)
Pyrite	3.30E-03	3.63E+02	3.75E+01	-3.72	Wiersma and Rimstidt (1984)
Siderite	3.30E-03	4.61E+02	5.34E+00	-10.65	Azaroual et al. (2002)
Smectite-high-Fe-Mg	2.00E-04	1.10E+03	5.32E+02	-12.02	set to montmorrillonite rate (Nagy, 1995)

3.3. DIFFUSION MODELLING OF CO_2 SATURATED FORMATION WATER IN THE CAPROCK TAKING INTO ACCOUNT REACTION KINETICS.

The section of the caprock that is likely to be affected by geochemical interactions due to the injection of CO_2 can be assessed by taking into account the diffusion process. Due to the slow progression of the diffusion process it is likely that the geochemical reactions will only occur in the lower section of the caprock.

With respect to the combined effect of diffusion and geochemical reaction, the caprock can behave according to three different "regimes":

- *Diffusion dominant*: diffusion is fast compared to mineral interaction, the movement of the dissolved CO_2-front is determined by the diffusion coefficient and it is unlikely that minerals will only get depleted at the base of the caprock within the timeframe of interest; the change in porosity is minor and spread over a large section. The CO_2-front is flattened off.

- *Reaction dominant*: diffusion is slow compared to mineral interaction, the movement of the CO_2-front is determined by the rate at which minerals, which trigger CO_2-trapping, get depleted in the section. The CO_2-front remains steep and will move extremely slow penetrating only the very base of the caprock. The intensive mineral reaction in these few meters can change the porosity significantly.

- *Mixed impact of reaction and diffusion*: this situation is intermediate between the two previous regimes, progression of the CO_2-front is determined by both the diffusion coefficient and mineral interaction.

3.3.1. Model description

The reaction transport model consists of two components:

- A transport component whereby CO_2 is transported from the CO_2 saturated formation water just below the base of the caprock into the caprock. The driver for this transport is diffusion, the rate at which CO_2 is transported is determined by the diffusion coefficient. The diffusion process is symmetrical in lateral direction and therefore only 1-dimensional vertical flow is modelled.

- A geochemical component, identical to the model described for the kinetic batch model.

The lower boundary of the column is defined as a constant concentration boundary, the upper boundary is defined as a constant flux boundary. The ideal timestep for the simulation depends on the mass transfer and is therefore determined by the rate of diffusion and the rate of the mass released by the geochemical reactions.

Only in the first cell a constant CO_2 fugacity is defined of 52. In all other cells no CO_2 is present at the start of the simulation.

3.3.2. Sensitivity of the diffusion coefficient

In order to assess the impact of diffusion coefficient on the diffusion transport of CO_2 into the caprock, the CO_2 penetration depth is simulated according to a range of diffusion coefficients. The diffusion coefficient values ranged between 10^{-10} m^2/s down to 10^{-14} m^2/s. The diffusion coefficient of CO_2 in water only is 1.8 10^{-9} m^2/s (20°C). When taking into account the shales with an estimated porosity of 5%, this value decreases according to Hellferich (1966) to a range of 4.5 10^{-11} m^2/s down to 1.18 10^{-12} m^2/s.

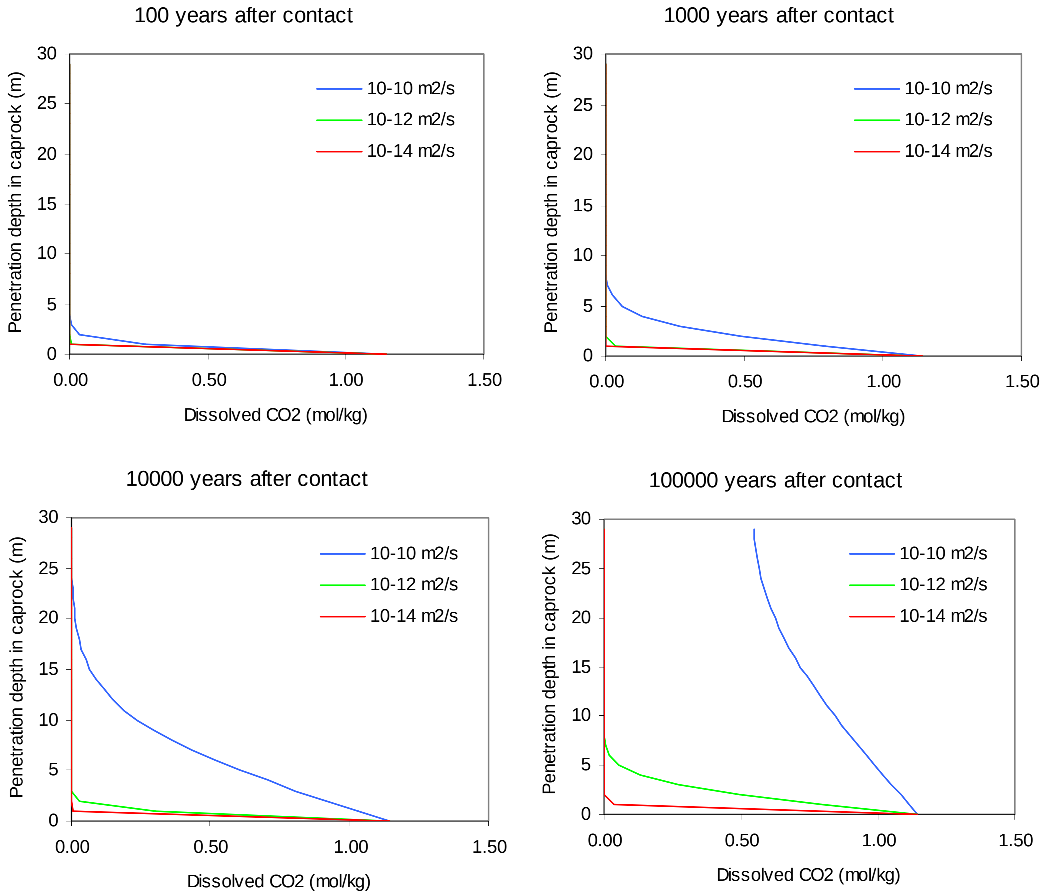

Figure 6 - Diffusion of CO_2 into the caprock: penetration depth versus dissolved CO_2 concentration in the caprock formation water after 100, 1000, 10000 and 100000 years of starting CO_2 injection based on three different diffusion coefficients.

The CO_2 concentration profiles indicating the CO_2 concentration versus penetration depth in the caprock after 100, 1000, 10000, and 100000 years are shown in Figure 6. The graphs show that significant diffusion is only likely to occur after approximately 1000 years and only if a very high diffusion coefficient is assumed. When considering a more realistic lower value for the diffusion coefficient of 10^{-12} m^2/s then even after 10000 years the CO_2 will not penetrate the caprock for more than 4 m, after 100 000 years this increases to approximately 7 m.

This sensitivity analysis indicates that geochemical interactions between the caprock and the caprock formation water saturated with CO_2 will only take place in the lower section of the caprock.

3.3.3. Diffusion modelling coupled to the geochemical reactions

Kinetic-diffusion modelling is computationally intensive. Therefore, the number of cells is restricted to 10 cells of 1 m each for this type of simulation. A timestep of 1.157 days (100 000 s) is used and a total time of 15 000 years is modelled. The small timestep is selected to allow the model to converge, but implies an extremely long calculation time of several weeks. The diffusion coefficient is set at $4.5\ 10^{-11}\ m^2/s$.

The results after 1000, 5000 and 15000 years for the reacting minerals, the pH as well as the porosity and the amount of CO_2 sequestered is shown in the Figures 7, 8 and 9 respectively. To illustrate the impact of the geochemical reactions on the progression of the CO_2-front, CO_2 profiles based on both diffusion-only calculations (left) and diffusion and mineral interaction concentrations (right) are shown at the top of each figure.

The progression of the CO_2-front into the caprock is determined by the rate at which the dissolution of anorthite, with the subsequent formation of kaolinite and calcite, occurs. Only if a cell is depleted of anorthite, high dissolved CO_2 concentrations will be able to build up in this cell. The alteration of albite is slower and the CO_2 concentration in the cell will increase before all albite has altered. In the first cell only some initial calcite dissolution takes place.

All anorthite in a 1 m section is dissolved in approximately 870 years. The front of high dissolved CO_2 concentrations, which remains steep, will therefore progress at a rate of approximately 1.15 m per 1000 years into the caprock. For this calculation the contribution of the alteration of albite is neglected.

The alteration of anorthite (and of albite to a lesser extend) induces a reduction in porosity of a few percentages at the base of the caprock. This reduction in porosity in the lower part of the caprock is not taken into account during the simulation and therefore the calculated diffusion is, on the long term when the porosity reduces significantly, slightly overestimated.

3.3.4. Conclusions

The rate at which the front representing high dissolved CO_2 concentrations progresses into the caprock is calculated to be around 1.15 m per 1000 years. This is considerably lower than the calculated rate based on CO_2 diffusion only without mineral interaction. This estimate is based on the assumption that the plagioclase described to be present in the caprock consists of a 50/50% mixture of albite and anorthite.

The alteration of anorthite occurs dominates over the diffusion process with respect to CO_2 movement. This has as a consequence that dissolved CO_2 is not able to penetrate deeper into the caprock as long as anorthite is present because all CO_2 reacts with the anorthite present. The alteration of anorthite and subsequent formation of kaolinite and calcite lead to a reduction in porosity. Within the 15000 year timeframe this reduction will only occur in a thin section at the base of the caprock

The rate of alteration of albite is of the same order as the diffusion process itself with respect to CO_2 movement. This means that CO_2 will diffuse further into the caprock, even if albite is still present in the lower section, but albite will dissolve in significant amounts. The reduction in porosity will take place over a larger section and will be less profound.

The critical reaction rate whereby the caprock switches from a geochemical reaction determined regime to a mixed diffusion/geochemical reaction regime is situated between rates at which the alteration of anorthite and albite occur.

This stresses again the need for accurate data on the initial composition of the feldspars into the caprock in order to obtain improved results.

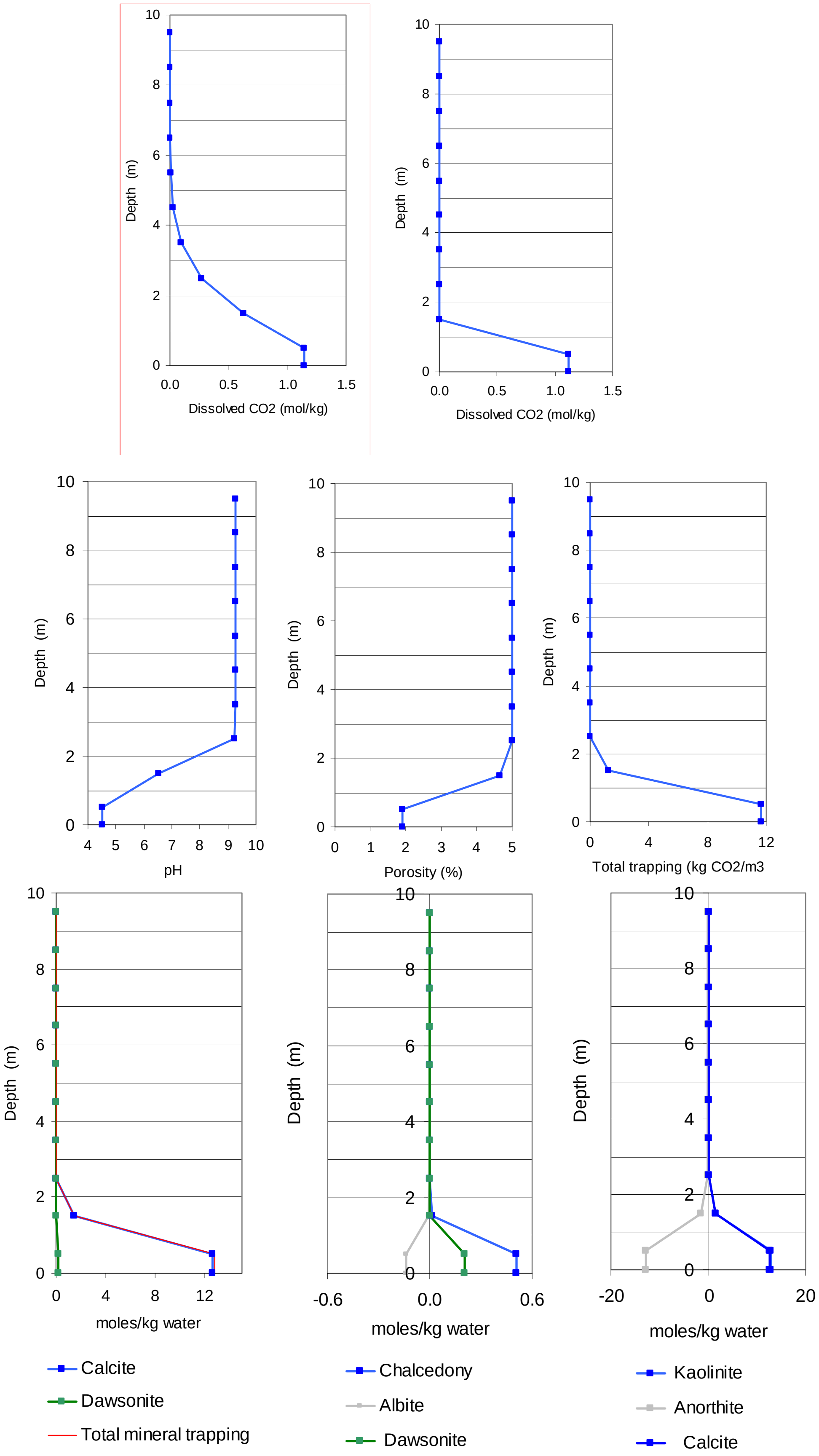

Figure 7 - Profiles of dissolved CO_2, pH, porosity, sequestered CO_2 and mineral changes in the lower section of the caprock 1000 years after CO_2-injection. The red bordered graph shows the dissolved CO_2-profile based on diffusion only.

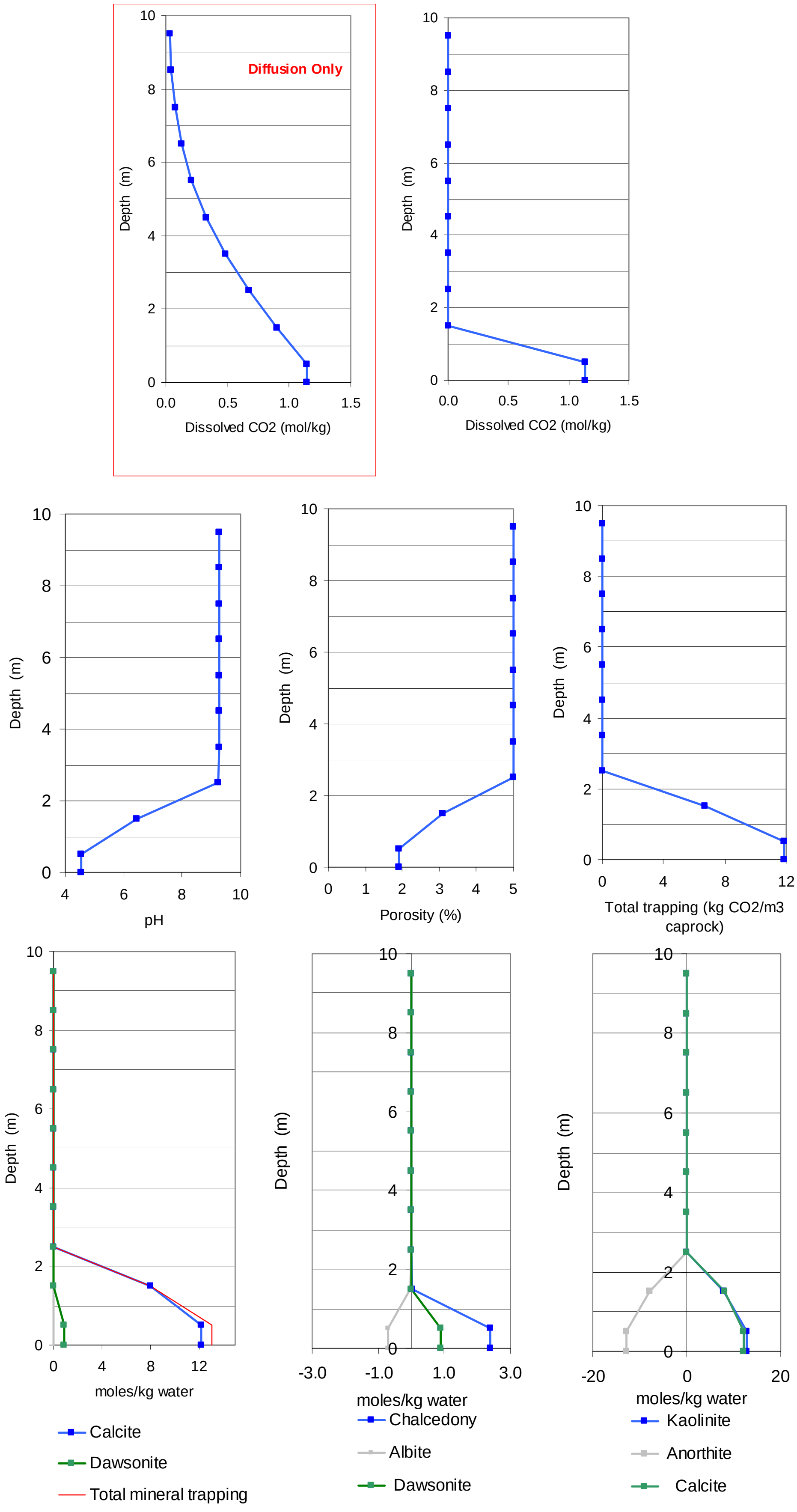

Figure 8 - Profiles of dissolved CO_2, pH, porosity, sequestered CO_2 and mineral changes in the lower section of the caprock 5000 years after CO_2-injection. The red bordered graph shows the dissolved CO_2-profile based on diffusion only.

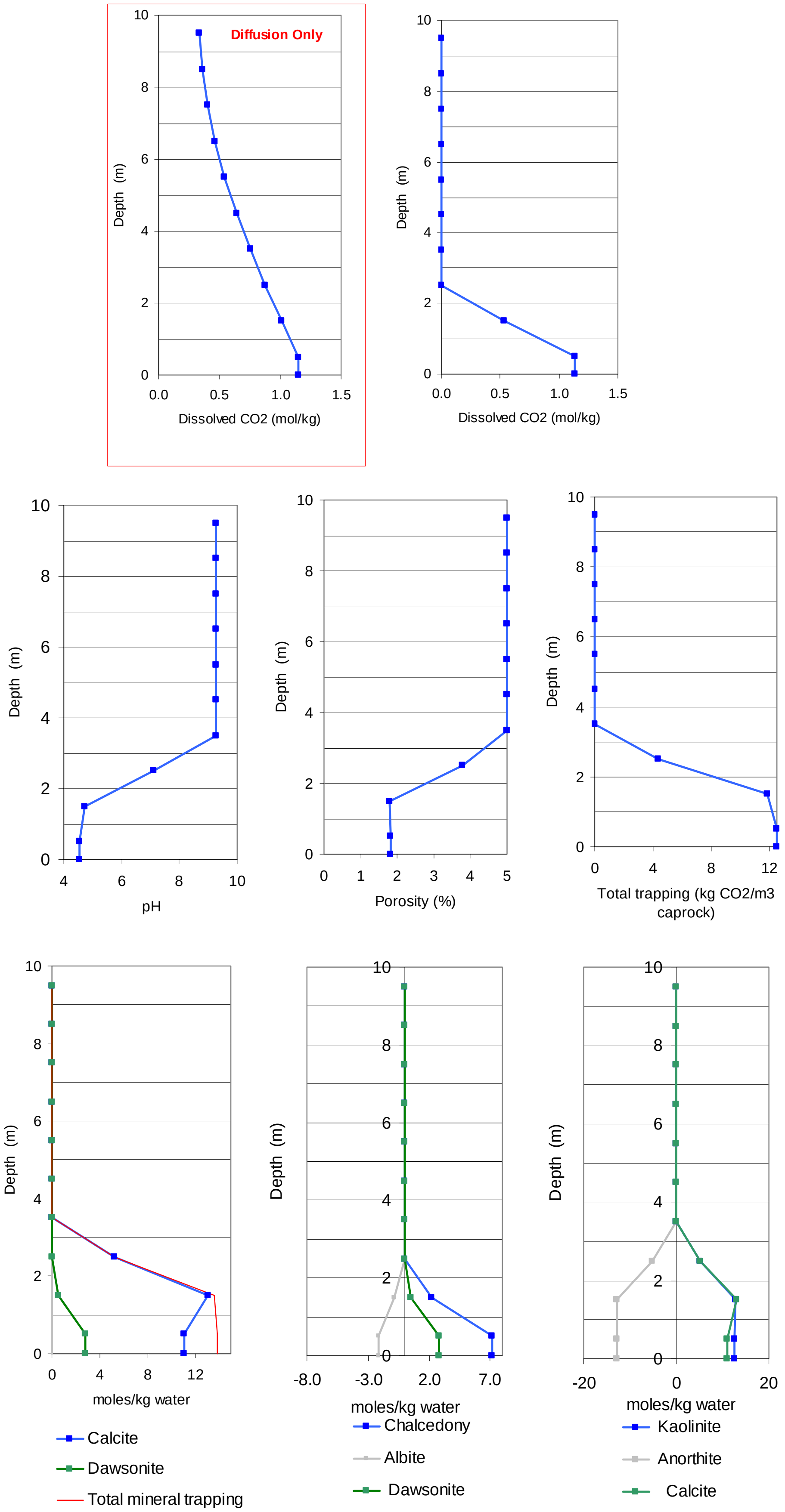

Figure 9 - Profiles of dissolved CO_2, pH, porosity, sequestered CO_2 and mineral changes in the lower section of the caprock 15000 years after CO2-injection. The red bordered graph shows the dissolved CO_2-profile based on diffusion only.

4. General conclusions

Four major conclusions can be drawn for this preliminary modelling with respect to the approach taken to model the long term impact of injection of CO_2 on the caprock. Although here specifically the conditions at Sleipner are modelled, certainly the first two conclusions will also apply to other (potential) CO_2-sequestration sites.

1.The modelling results clearly show that the impact on the porosity of the caprock due to geochemical interactions is very sensitive to two groups of parameters:

- the mineralogical composition of the caprock, including their availability to take part in geochemical interactions and the composition of solid solutions (here clearly illustrated for the plagioclase composition);
- the kinetics of crucial mineralogical interactions including their rates, pH–dependency, reactive surface area and the kinetic rate law itself.

Also thermodynamical parameters influence the changes in porosity, but thermodynamic mechanisms are better understood and their parameters are generally estimated with a higher accuracy than kinetic parameters.

2. Even for long term impact assessment the equilibrium approach is unlikely to be successful in predicting changes in porosity. When comparing the results from the equilibrium and the kinetic modelling after 15000 years (although minor differences in initial mineral composition are present) it becomes obvious that after 15000 years the system is still not at all in an equilibrium state and major mineral reactions modelled using the equilibrium assumption do not occur during the first 15000 years of the kinetic modelling.

3. This preliminary kinetic modelling suggests a reduction in porosity of the base of the caprock in the order of 3 % and a CO_2-sequestration capacity of 14.0 kg CO_2 per 1000 kg caprock over a 15000 years period.

4. The kinetic and diffusive transport approaches indicate that the impact of CO_2-injection on the caprock is limited in space. After 15000 years only the base of the caprock (in this case the bottom 3 m section) will be affected by CO_2-rich formation waters.

At this stage, it is unclear how robust the obtained results are: very small changes in some parameter values (selection of primary or secondary minerals, reaction rates, etc) can potentially lead to large variations in mineralogical transformations and porosity change. Estimating the robustness and the accuracy of the modelled results is crucial and requires detailed sensitivity analysis. Performing this analysis will be one of the challenges in the CO_2-STORE project.

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