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# Modelling CO<sub>2</sub>-induced fluid-rock interactions in the Altensalzwedel gas Reservoir. Part I - From experimental data to a reference geochemical model

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## Abstract

Modelling fluid-rock interactions induced by CO<sub>2</sub> is a key issue when evaluating the technical feasibility and long-term safety assessment of CO<sub>2</sub> storage projects in deep formations. The German R&D programme CLEAN (CO<sub>2</sub> Large-Scale Enhanced Gas Recovery in the Altmark Natural Gas Field) investigated the almost depleted onshore gas reservoir located in the Rotliegend sandstone at over 3000 m depth. The high salinity of the formation fluids and the elevated temperature in the reservoir exceed the validity limits of commonly available thermodynamic databases needed for predictive geochemical modelling. In particular, it is shown that the activity model of Pitzer has to be applied, even if necessary input data for this model are incomplete or inconsistent for complex systems and for the considered temperatures. Simulations based on Debye-Hückel activity model lead to severe, systematic discrepancies already in the simple proposed reference case where experimental data could be used for comparison. A simplified geochemical model, consistent with the average measured composition of formation fluids and the prevailing mineralogical assemblage of the host rock, identifies the mineral phases most likely to be considered at equilibrium with the formation fluid. The simulated reactions due to CO<sub>2</sub> injection, under the hypothesis of local thermodynamical equilibrium, result in a moderate reactivity of the system, with the dissolution of anhydrite cementation and hematite being the most relevant expected mineral reactions. This is compensated, at equilibrium, by the precipitation of new carbonates like calcite and siderite, for an overall very small loss of porous space. The simulated rather small effect of mineral alteration is also due to the scarce amount of water available for reactions in the reservoir. The results of the model are qualitatively in line with observations from batch experiments and from natural analogs.

**Keywords:** CO<sub>2</sub> storage, geochemical modelling, high salinity, Pitzer model, CO<sub>2</sub> solubility

In the framework of the German R&D programme CLEAN (CO<sub>2</sub> Large-Scale Enhanced Gas Recovery in the Altmark Natural Gas Field), the injection of CO<sub>2</sub> in a depleted gas reservoir was investigated (Kühn et al, 2011, this issue). In this paper we present a simplified hydro-geochemical model representative of the considered reservoir and assess the reliability of the obtained results. This model constitutes the basis upon which kinetics and reactive transport modelling will be performed, as shown in part II (Beyer et al, this issue).

The complexity and variability of natural media can only be partially described by numerical models. This is particularly true for geochemical simulations of fluid-rock interactions in deep formations, where the parameters relating to the high salinity of fluids represent a major difficulty (Duan et al, 2006; Marini, 2007; Zhang et al, 2009; Gaus, 2010). A significant general assumption has to be pointed out: geochemical modelling deals with aqueous chemistry, and uses the methods developed for electrolyte solutions, therefore neglecting direct gas-rock interactions. This is a quite adequate assumption for two reasons: firstly, the water phase is ubiquitous in porous media, even if in an adsorbed - immobile - state as in a gas reservoir. In addition, for the considered sandstones, water constitutes the wetting phase (Pudlo et al, this issue), therefore physically hindering direct CO<sub>2</sub>-rock contact as long as a film of adsorbed water is present on the pore walls. Secondly, gas-rock reactions are orders of magnitude slower than in the presence of water, and get relevant only in particular cases, such as the carbonation of borehole portlandite cements (Regnault et al, 2009).

The chemical composition of the formation fluid and the mineral assemblage of the host rock, as experimentally obtained, are the object of the below section 1. A comparison of the outcome of different thermodynamic databases is given in section 2, and “benchmarked” against precise experimental data about the solubility of CO<sub>2</sub> in a NaCl brine. Unfortunately it is currently not possible to directly validate the models against experimental data for complex systems and high concentrations and temperature. Finally, a representative initial model for the targeted reservoir is proposed and showed to match at least qualitatively the experimental evidences as resulting from CO<sub>2</sub> exposure of core samples.

The reference simulator for this study is the well known program PHREEQC, internally based on the law of mass action (Parkhurst and Appelo, 1999).

## 1 Available data

The degree of knowledge of the Altensalzwedel compartment of the Altmark gas field (Saxony-Anhalt, central Germany) is relatively high, given the amount of data collected from boreholes drilled during the production history and additional analyses on cores and fluid samplings specifically performed in the framework of the CLEAN project.

The reservoir is located in a Rotliegend sandstone at over 3000 m depth, with a temperature of about 120 °C. The reservoir rocks mainly consist of sandstone and siltstone and, in minor proportions, clay layers, with salt beds occurring in the upper parts of the reservoir along with siltstone and claystone. The reservoir is covered by a massive Zechstein salt cap rock and underlain by Permian volcanic rocks. There is no evidence of intrusion of fluids from near formations as result of the depletion: the Altensalzwedel subfield is considered hydraulically isolated. The reservoir is also considered dry, meaning that the wetting aqueous phase is almost immobile and residual saturation prevails at least in the conductive horizons of the reservoir. The residual brine saturation was estimated to be in the range 20-40%. The current pore pressure in the reservoir is around 45 bar, depending on the considered well and layer; it exceeded 400 bar at the beginning of production. The composition of the nowadays produced gas is about 75 % N<sub>2</sub>, 25 % CH<sub>4</sub>, with small amounts of CO<sub>2</sub> (mass fraction below 1 %) and smaller amounts of other more complex hydrocarbons. The presence of such a low pristine CO<sub>2</sub> partial pressure is taken into account when evaluating the hypothesis of geochemical equilibrium with the host rock (cfr sec. 3.1).

However, the reactivity of the system will increase dramatically due to the injection of CO<sub>2</sub>, increasing its partial pressure from a fraction of a bar to around 50; this will considerably enhance further fluid-rock interactions. Therefore the host rock cannot be considered at equilibrium with CO<sub>2</sub> like in other comparable reservoirs, such as K12B, with a much higher initial content of CO<sub>2</sub> (Audigane et al, 2009).

### 1.1 Formation fluids: analysis from samples

In the framework of the project CLEAN, GDF SUEZ E&P DEUTSCHLAND allocated around 30 previously generated chemical analyses of formation fluids collected at separators during the production of the reservoir, as well as recently performed sampling campaigns of deep fluids. Further independently published analyses referring to the same Altensalzwedel compartment and other adjacent subfields, all in the same Rotliegend formation, can be found in Lüders et al (2010). The available analyses, which can be only partially related to specific depths of the reservoir, show a high variability in overall salinity, ranging from 240 to about 370 g/l, with an average of approximately 340 g/l. This appears to be the most representative value, emerging also from other Rotliegend reservoirs at analogous depth.

The chemical composition of the formation water is clearly dominated by Cl, Na, Ca and K, with Mg, Mn and Br also present in considerable amounts, as well as dissolved Fe. The brine is slightly acidic, and anoxic conditions are assumed. Table 1 summarizes the reference chemical composition as resulting from a recent (2009) analysis of the formation fluid along with a re-evaluation performed using the chemical simulator PHREEQC and a reference Pitzer database; refer to section 3 for further details about modelling and used database.

### 1.2 Mineralogical composition of host rock from core samples

Facies, mineralogical, geochemical, and petrophysical analyses on material from the Altensalzwedel Rotliegend sandstone are described in detail by Pudlo et al (this issue). Here we summarize its most distinct characteristics for the definition of a representative geochemical model.

Microscopic and analytical investigations, completed by a description of depositional environment and lithofacies types, reveal a playa-/sebkha-like environment, dominated by aeolian (aeolian dunes, dry sand flats) and fluvial (fluvial/aquatic) sediments. The modal composition of the sandstones is dominated by quartz (60-65%), and includes K-Feldspar and volcanic lithoclasts, pore-filling calcite/anhydrite cements and hematite-bearing illitic-chloritic grain coatings.

Samples from both main lithotypes (aeolian, fluvial/aquatic) show signs of alteration (bleaching) which appreciable changes in color, from reddish for unaltered sandstones, to white to grey in the bleached rocks.

The proposed alteration of red bed into bleached sandstones is reflected in an enhanced dissolution of feldspar lithoclasts, pore-filling calcite/anhydrite cements and of hematite-bearing illitic-chloritic grain rimming coatings. Mineral precipitations most probably related to fluid-rock interactions comprise the formation of Fe-poor chlorite, illite, Mn- and Fe-enriched calcite, and of REE-enriched carbonate (synchisites). Thus these altered sandstones are classified as the diagenetic C-rock type of Gaupp (Gaupp, 1996), which commonly resembles most favourable reservoir qualities due to their high porosity and permeability, originating from preferential dissolution of cement-forming mineral phases during burial diagenesis.

In contrast, the calcite, anhydrite, and hematite-enriched red bed sandstones possessing low porosity and permeability suffered only limited mineralogical modifications during the diagenetic processes (Pudlo et al, this issue).

These observations suggest a major control of late diagenetic fluid-rock reactions on rock alteration at depths, most pronounced in the well sorted, bleached aeolian sandstones, enabling enhanced fluid flow rates. Consequently, this lithotype is considered to be the most important for CO<sub>2</sub> migration.

Table 1: Representative analysis of formation fluid. Sampling and analysis performed by GDF SUEZ E&P DEUTSCHLAND, 2009; re-evaluation using PHREEQC and the Pitzer database provided by Quintessa ltd.

Parameter	Analysis	Re-evaluated with PHREEQC/Quintessa		Included in model
pH	5.5	4.8		
density	1.239 g/cm <sup>3</sup>			
TDS	351 g/L			
	<b>g/L</b>	<b>g/L</b>	<b>mol/kgw</b>	
Al	Not measured	1.89E-7	7.88E-9	<i>x</i>
B	0.22	0.22	0.0229	
Ba	0.14	0.14	1.15E-3	
Br <sup>-</sup>	0.58	0.58	8.16E-3	
Σ C	0.013	0.016	1.20E-3	<i>x</i>
Ca	50.20	50.2	1.41	<i>x</i>
Cl <sup>-</sup>	215.60	215	6.84	<i>x</i>
Fe	0.59	0.406	8.2E-3	<i>x</i>
K	6.20	2.56	0.074	<i>x</i>
Li	0.39	0.39	0.063	
Mg	0.77	0.77	0.0356	<i>x</i>
Mn	0.94	0.94	0.0192	
Na	71.4	73.4	3.60	<i>x</i>
Pb	0.10	0.10	4.83E-4	
SO <sub>4</sub> <sup>2-</sup>	0.0893	0.097	0.00192	<i>x</i>
Si	Not measured	8.98E-3	3.63E-4	<i>x</i>
Sr	1.90	1.90	0.0244	
Zn	0.38	0.38	6.53E-3	
Ionic Strength (calc)			7.5	

Table 2: Average modal mineralogical composition (in volume percent) of the core samples analyzed by Pudlo et al (this issue), aggregated per lithotype and alteration state. Aeolian sandstones show more frequent bleaching and enhanced porosity and permeability, based on non-systematic sampling.

<b>Lithotype Alteration</b>	Aeolian		Fluvial/Aquatic		<i>At equilibrium in initial model</i>
	Grey	Red	Grey	Red	
n. samples	42	5	18	18	
Quartz	61.44	58.28	61.59	57.28	
Anhydrite <sup>1</sup>	9.25	19.20	8.88	15.79	x
Calcite	2.24	3.00	3.92	5.14	x
K-Feldspar	6.10	4.56	7.34	5.82	x
Anorthite	2.32	1.88	2.23	1.41	
Albite	0.93	0.24	1.54	0.58	x
Fe-Chlorite	2.68	1.52	2.66	1.07	
Fe-Illite <sup>2</sup>	0.86	0.76	0.79	0.64	x
Hematite	0.12	1.88	0.40	1.17	x
<i>Others</i> <sup>3</sup>	8.21	8.32	8.33	10.49	
Porosity	5.85	0.36	2.31	0.61	

<sup>1</sup> The designation *Anhydrite* comprises all sulphate phases (gypsum, barite)

<sup>2</sup> Illite-IMt\_2, after Gailhanou et al. (2007)

<sup>3</sup> *Other* mineral phases are principally mafic and volcanic lithoclasts, Fe-Ti-oxides, other clay minerals and REE-enriched carbonates

Table (2) summarizes the average mineralogical composition of the analyzed samples, aggregated per lithotype and alteration state. Only about 10% of the samples taken from the aeolian sandstone were red (unbleached); in contrast, the proportion of red and grey samples for the aquatic/fluvial lithotype is 1:1. However, as the sampling is not systematic, such proportions may not reflect the real distribution in reservoir, and therefore can only be regarded as a rough estimation.

## 2 Geochemical Modelling

### 2.1 Thermodynamic databases

The set of thermodynamic constants describing the equilibrium state of aqueous and mineral reactions has to be consistently compiled over a defined range of temperature, pressure and *ionic strengths*<sup>1</sup>. A major role in the consistency issue is played by the underlying *activity model*. The distinction between *activity* and *concentration* of solute species accounts for the *non-ideal* behavior of real, concentrated solutions. The theory of Debye and Hückel (Merkel et al, 2005) forms the fundamental theoretical framework for the derivation of activity corrections. It considers the ions as spheres of radius  $\bar{a}$ , and approximates the activity coefficients with the equation:

$$\ln \gamma_i = -Az_i^2 \frac{\sqrt{I}}{1 + B\bar{a}\sqrt{I}} \quad (1)$$

where  $A$  and  $B$  are two temperature-dependent constants,  $z_i$  is the specific ion's charge and  $I$  is the ionic strength; it follows that the activity coefficient for each species depends on the actual speciation of the

<sup>1</sup>The ionic strength constitutes a measure of non-ideality of a concentrated solution, and is defined as:  $I = \frac{1}{2} \sum_i z_i^2 C_i$ ;  $C_i$  is the concentration in moles per kg water and  $z$  the specific charge of the  $i$ -th solute species.

solutions, *via* the  $I$  term. The original Debye-Hückel theory is valid for moderate concentrations (not exceeding 0.1 mol/kgw). Several extensions and approximations based on the Debye-Hückel theory have been presented in literature in order to extend the validity of the equation up to 2-3 molal, and even further for Na-Cl dominated solutions; among them, the Davies equation (Davies, 1962), the b-dot equation, the Truesdell-Jones equation (Truesdell and Jones, 1974). A thorough overview is given in (Dethlefsen et al, 2011).

In the range of validity of extended Debye-Hückel formulations, reliable data are available for a large number of minerals and aqueous reactions, including redox reactions, and over a very large range of temperatures. In particular, the LLNL database (Johnson et al, 1992; Wolery, 1992), provided with the standard code PHREEQC, is valid in the range 0-300°C and is therefore adopted by a number of modellers also for CO<sub>2</sub> applications (Gaus et al, 2005; Wigand et al, 2008).

For the specific case studied in this paper, as well as for a great number of other CO<sub>2</sub> storage applications in deep formations, the fluids are extremely saline, with ionic strength indicatively in the range of 4 to 8 mol/kgw. In these cases more complex theoretical models should be considered, such as the specific ion interaction model developed by Pitzer and coworkers (Pitzer, 1973; Harvie et al, 1984). This theory is adapted to describe electrolyte solutions up to very high ionic strengths; in practice, however, given the difficulty linked to the experimental determination of Pitzer coefficients, model's parametrization is incomplete or inconsistent for complex systems, lacking relevant specific interactions, mainly involving Al and Si compounds; furthermore, temperature dependence of parameters is inconsistently measured for temperatures higher than 25 °C. Ongoing efforts in the scientific community are trying to provide better data for the Pitzer activity model and new data are continuously being published (Christov et al, 2007; Accornero and Marini, 2009).

Of particular interest in this regard is the project-specific compilation of thermodynamic and Pitzer data performed by the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) (Moog and Mönig, 2010) and made available for both the chemical codes PHREEQC and CHEMAPP (Peterson and Hack, 2007), which is based on Gibbs' Energy Minimization. Therefore the GRS database ensures consistent results between simulators. This database includes data for the system Al-C-Ca-Cl-Fe-H-K-Mg-Na-S-Si.

A second extensive compilation is the EQ3/6 database (Wolery, 1992), specifically developed at Sandia National Laboratory for the Yucca Mountain radioactive waste project and translated to PHREEQC format by Quintessa Ltd (Benbow et al, 2008). Both Pitzer databases comprise relevant Al and Si compounds, thus enabling geochemical simulations involving aluminosilicates. However, it has to be pointed out that both are not consistently parametrized for temperatures above 25 °C and their thermodynamic data for aqueous and mineral reactions are collected from heterogeneous sources; nonetheless, to our knowledge they represent the state of the art regarding Pitzer data. We intentionally did not incorporate in the databases the most recently published re-evaluations or new data of specific interaction parameters, *i.e.* Accornero and Marini (2009), because this would have required a refit of several involved equilibrium constants, which was beyond the scope of this work. In the following, we will refer to the two original databases with the name of the compilers, GRS and Quintessa respectively.

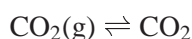
Uncertainties and errors in the underlying chemical and thermodynamic databases propagate to the results of simulations. Computational analysis of such propagation in a setup similar to that of the Altmark reservoir showed that an assumed relative error of 5% in the Pitzer coefficients for relevant compounds, which at elevated temperature is a realistic estimation, can lead to discrepancies in the results of simulations exceeding 15%

Another issue is the dependency on pressure of the reactions' equilibrium constants. PHREEQC, like other hydrogeochemical codes, disregards such effect, which means that thermodynamic databases are compiled for the standard pressure of 1 bar (or water saturation pressure for higher temperatures). One chance to evaluate the effective influence of pressure is offered by software packages such as SUPCRT92

(Johnson et al, 1992) or CHNOSZ (Dick, 2008), which use empirical correlations and advanced equations of state to derive molar properties of minerals and solute compounds for a specific T and P. The problem is, that those rely on other thermodynamic databases (sprons98, dprons98, obigt just to cite the best known) and therefore can introduce a further source of error or inconsistency because of the mixing of different data sources. However, a systematic numerical evaluations with the software package CHNOSZ showed that the variation of mineral formation equilibrium constants ( $\log_{10} K$ 's) from 1 to 200 bar is of second order compared to the uncertainty linked to the activity calculation, and really negligible in the expected operative pressure for the EGR scenario in the Altensalzwedel reservoir.

## 2.2 Solubility

The phase equilibrium between the CO<sub>2</sub>-rich phase and the aqueous phase is the process which initiates the chemical interactions between CO<sub>2</sub> and rock; it is intrinsically a chemical process, and is influenced by temperature, pressure and chemical composition of the brine. In terms of chemical equations the phase equilibrium is expressed by the reaction:



Henry's law states that, at equilibrium, there is proportionality between *partial pressure* of gaseous CO<sub>2</sub> and the concentration of its dissolved species. For higher pressures, temperatures and salinities there is a need to account for non-idealities, which means to consider **fugacity** instead of partial pressure, activity instead of concentration, and to apply another correction term, usually referred to as "Poynting term" (Duan et al, 1992; Spycher and Pruess, 2005). Basic thermodynamical considerations lead to the equation (Spycher et al, 2003; Gottschalk, 2007):

$$a_{\text{CO}_2(\text{aq})} = \frac{\varphi_{\text{CO}_2} P_{\text{CO}_2}}{K_H} \cdot \exp \left\{ -\frac{\bar{v}_{\text{CO}_2}}{RT} (P_{\text{CO}_2} - 1) \right\} \quad (2)$$

where  $\bar{v}_{\text{CO}_2}$  is the average molar volume of aqueous CO<sub>2</sub>(aq) over the P range [1, P<sub>CO<sub>2</sub>],  $K_H$  is the Henry constant and  $\varphi$  is the *fugacity coefficient* of (gaseous) CO<sub>2</sub>, which can be calculated from an equation of state (EOS) for pure CO<sub>2</sub>. Given its accuracy, the 5th order virial EOS for CO<sub>2</sub> of Duan Møller Weare (Duan et al, 1992) is recommended over other cubic EOS (Peng-Robinson and Soave-Redlich-Kwong being the most cited in literature).</sub>

Equation 2 determines the activity of dissolved CO<sub>2</sub> as a function of temperature and pressure; the actual concentration, the physical amount of CO<sub>2</sub> dissolved in the solution is proportional to the activity coefficient, which is in turn a function of the ionic strength of the solution. Again, the model of activity correction is crucial for concentrated solutions.

A straightforward way to check the influence of the activity model when considering equation 2 is to compare the results of PHREEQC simulations with different databases to experimental data and reference models. Given the need for extreme high salinities (over 6 molal), reliable solubility data are to be found in literature only for the system H<sub>2</sub>O-NaCl-CO<sub>2</sub> - refer to the extensive evaluation of solubility data in Duan et al (2006). Figure 1 thus compares the aqueous concentration of dissolved CO<sub>2</sub> calculated with PHREEQC using expression 2 based on a Pitzer ion interaction model (Quintessa database), on an extended Debye-Hückel model (LLNL database), along with experimental data measured by Rumpf et al (1994) and the reference Duan-Sun solubility model, which is also internally based on a simplified Pitzer formalism (Duan and Sun, 2003). It is clear from the picture that the Pitzer-based PHREEQC simulations have the same accuracy as the Duan-Sun model, in a broad range of temperature, pressure and salinity, while Debye-Hückel simulations show more severe systematic discrepancies with respect to the experimental data. Such discrepancies are expected to increase even further for non pure Na-Cl solutions, as in most natural systems, suggesting the inadequacy of other activity models than Pitzer's. In particular, since the activity coefficients in Debye-Hückel-based models tend to be underestimated



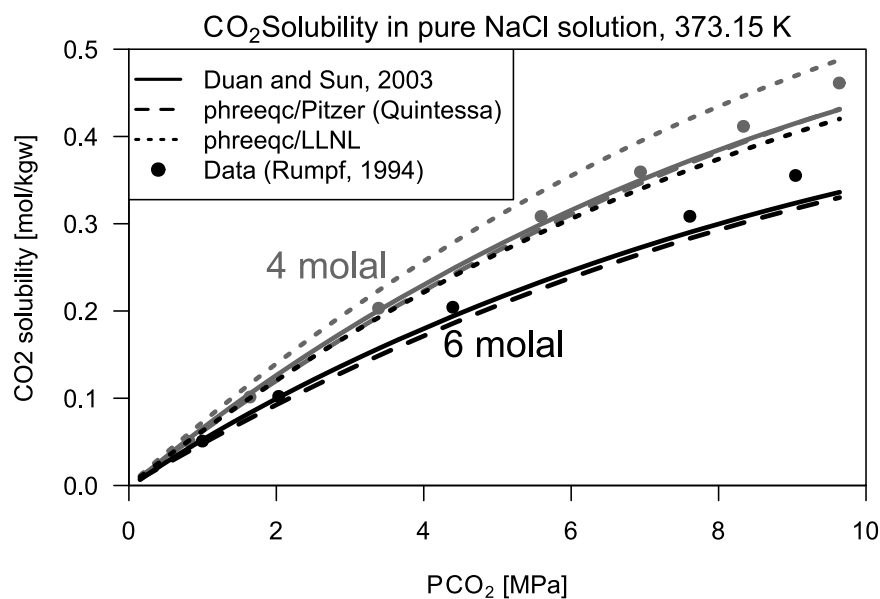


Figure 1: Calculated solubility of CO<sub>2</sub> in an aqueous Na-Cl solution, compared to reference Pitzer-based solubility model and experimental data. PHREEQC calculations based on Debye-Hückel model (LLNL database) show a systematic overestimation with respect to experimental data for the considered ionic strengths, 4 and 6 molal.

with increasing ionic strengths, it follows that such models overestimate the actual concentrations, that is the real amount of dissolved CO<sub>2</sub>.

### 3 Results

#### 3.1 Definition of representative initial state

The re-evaluation of the measured hydrochemical composition of the brine - including also minor elements - was possible only with the LLNL and Quintessa databases, because several of these elements are not included in the GRS database. Since the Pitzer model has to be preferred for the reasons explained in the previous section, the results from the calculation with Quintessa database are given as reference in table 1.

Among the mineral phases listed in table (2), an averaged assemblage consisting of K-feldspar, albite, Fe-bearing illite (thermodynamic data from Gailhanou et al (2007)), hematite, and a pore-filling cementation constituted by calcite and anhydrite was found to match the hypothesis of equilibrium with the formation fluid, and was therefore taken as initial state for the geochemical modelling. Such assemblage of primary mineral phases is common to both lithotypes and, to a certain extent, to their alteration state. Given the quality of the available thermodynamic data, it is not possible to represent in the models the mineralogical and geochemical variability experimentally observed. Exemplary is the distinction between fibrose and cutan Fe-bearing illites, or the REE- and Fe- enriched calcite. As pointed out in section (1) it is also unrealistic to quantitatively estimate the extent of bleaching in the sandstones. However, taken the good correlation between porosity, permeability, lithotype and proportion of altered samples (Pudlo et al, this issue), also confirmed by *history matching* of production data through dynamical modelling performed by the operator, the aeolian bleached sandstone should be clearly given the highest specific weight in a hypothetical weighted average, being the most likely to receive the major amount of CO<sub>2</sub>. Once that said, the mineralogical and geochemical variability between lithotypes and

between the bleached and not bleached sandstones will be described, in a geochemical model, only by different proportions of the same mineral phases.

Reducing conditions are assumed in the model ( $p_e = -1.5$ ) in order to match the amount of observed dissolved Fe, with  $Fe^{2+}/Fe^{3+}$  being the governing redox couple for the system. Other mineral phases, which have been observed in the core samples, like Fe-bearing chlorite (chamosite), are oversaturated in the fluid, but not included at equilibrium in this model to prevent massive Mg precipitation and therefore its removal from the solution; this could be a hint pointing to the kinetic limitation of the reaction involving chlorite. The same consideration applies to K-feldspar, also oversaturated in the fluid. After Lüders et al (2010), the K concentrations of the brines in the Altmark Rotliegend are compatible with the values expected solely from an increase in salinity due to seawater evaporation, and there are no other signs of relevant enrichment descending from water-rock-interactions. However, Pudlo et al (this issue) found evidence of albitization of K-feldspar in Altensalzwedel core samples as well as illitization of smectite, reactions who would control the K concentration. Therefore we considered the fluid at equilibrium with both illite and K-feldspar, which gives a dissolved K concentration slightly smaller than the observed. A small partial pressure of gaseous CO<sub>2</sub> was applied, around 0.5 bar, corresponding to the actual CO<sub>2</sub> mass fraction in the reservoir, which fixes the pH and the content of inorganic dissolved carbon. The geochemical effects of organic material and of the other gases present in the reservoir (nitrogen and methane, mainly, as listed in section 1), i.e. on the redox potential, were neglected.

The reference model of mineral assemblage and fluid composition described above, without of the elements B, Ba, Li, Mn, N, Pb, Sr and Zn, which are not comprised in the GRS database, but with the same primary mineral phases at equilibrium, was taken as benchmark for the comparison between the results yielded by the three considered databases (figure 2). The difference in calculated ionic strength caused by the simple removal of these elements from the solution is less than 0.5 molal. Major discrepancies between both Pitzer-based and the LLNL database appear the very high activities calculated with the LLNL's of the neutral aqueous species such as NaCl, KCl and CaCl<sub>2</sub>, which in that case account for a relevant part of total dissolved K, Cl and Na. Such species are not defined at all in the Pitzer databases, with the exception of CaCl<sub>2</sub> in Quintessa's. As result of this difference, the activities of major aqueous species such as Ca<sup>2+</sup>, Cl<sup>-</sup> and Na<sup>+</sup> varies in a range of one order of magnitude over the three databases. This discrepancy also reflects in the calculated ionic strength, at equilibrium, which is around 5.5 for the LLNL database and above 7 for the Pitzer-based databases. This result is quite conclusive about the practical inadequacy of extrapolating reasonable results from Debye-Hückel simulations for the specific case. One solution could be to exclude those neutral species from the LLNL database. This results in a increase in the calculated ionic strength and in general a less pronounced discrepancy with the outcome of Pitzer databases.

### 3.2 Mineral alterations after exposition to CO<sub>2</sub>: batch simulations

Given the nature of the gas reservoir, where formation water is present practically only in residual saturation, hence virtually immobile, batch simulations are expected to capture at least qualitatively the effect of the injection of dry CO<sub>2</sub> into the reservoir. In fact, no relevant mass transport of reactive species other than the migration of the CO<sub>2</sub>-rich phase itself and salt precipitation due to dry-out (limited locally around the injection well) are expected. Other fluid-fluid interactions like fractionation of dissolved elements into the gaseous CO<sub>2</sub> stream can be realistically estimated for a marginal elemental transport at reservoir scale, since it is not expected to alter significantly the concentration of soluted species (Rempel et al, 2011).

The dry-out of formation waters around the injection well lead to precipitation of salts which could clog the porous media and severely reduce the injectivity of the well. Since this research is still ongoing and this matter does not fit in the scope of the present paper, only preliminary results and considerations are given here.

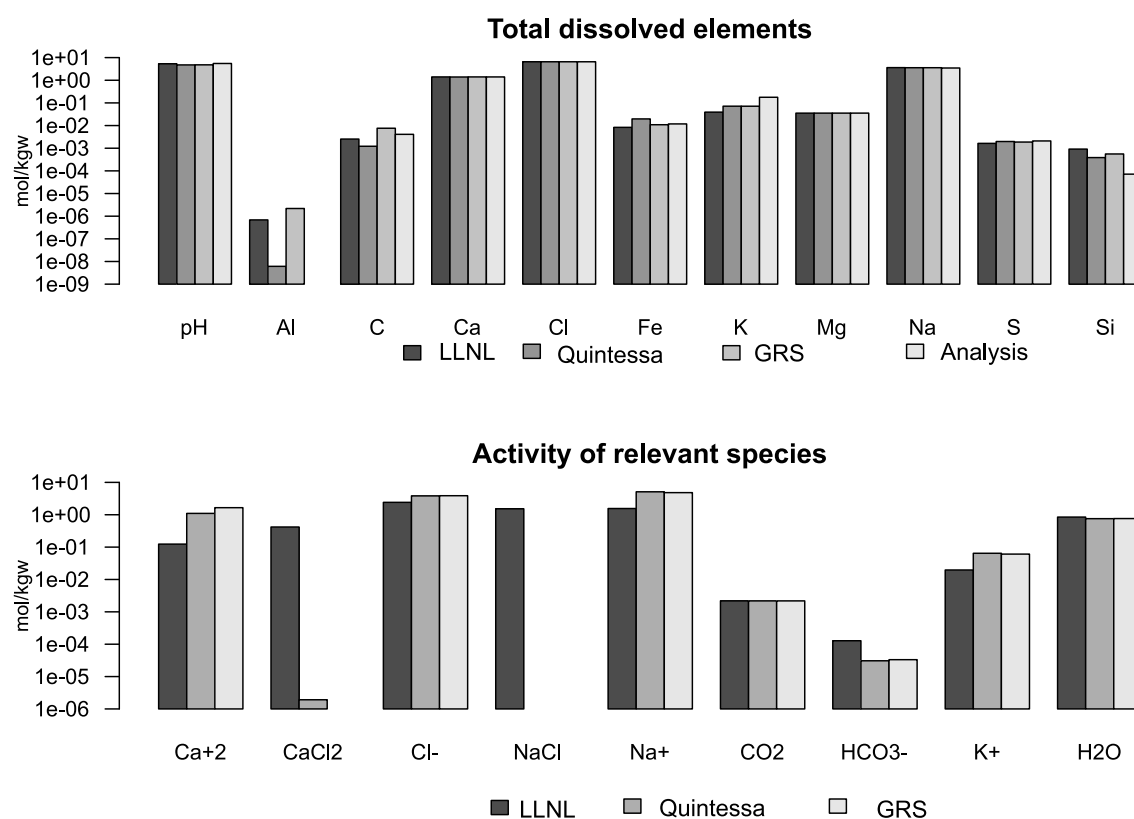


Figure 2: Comparison of reference initial states calculated with three different databases: Quintessa and GRS, based on Pitzer activity model, and LLNL, based on Debye-Hückel. For the considered ionic strength, the LLNL calculations seem implausible particularly regarding the non charged ions like aqueous NaCl and CaCl<sub>2</sub>.

The simulation of evaporation processes is quite challenging for fluids such as those of the Altmark, since the concentrations of solute species increase dramatically and reach ionic strengths of 20-25 molal. Under these conditions, the geochemical calculations become quickly not reliable, resulting in the misprediction of which salt would precipitate and severe mass balance or electroneutrality errors. Under Altmark conditions, simplified model considering only major ions and the corresponding salts (Sylvite - KCl, Hydrophilite - CaCl<sub>2</sub> and Halite - NaCl) predict the precipitation of 82 cm<sup>3</sup> of salt per liter of initial formation fluid; a theoretical analytical calculation leads to 146 cm<sup>3</sup>. The total pore volume available to gas flow is thus overall increased. This figure does not consider capillary effects which could replace the evaporated brine thus locally increasing the precipitated salt amount. Considering an initial porosity of 15 % and brine saturation of 30%, a rock volume has to be flushed at least around 1,500 times with dry CO<sub>2</sub> to theoretically reach the complete evaporation of water phase. Thus, salt deposition due to dry-out is likely to propagate just for few decameters - at the farthest - from injection well.

Batch simulations under the hypothesis of instantaneous equilibrium depict to some extent a *worst case* scenario, where all the available mineral phases are allowed to participate simultaneously to the chemical reactions, and have to be read as qualitative results. The focus here is on the thermodynamic data and on the plausibility of the achievable simulations under the challenging conditions of extremely high salinity and temperature above 100 °C. To proceed towards a realistic quantitative approach, kinetics and coupled reactive transport models need to be considered, and for this specific case are described in Beyer et al (this issue).

Natural analogs of geological CO<sub>2</sub> storage in comparable Rotliegend reservoirs can give insights about the expected reactions to be included in the geochemical models: a thorough review is given in Ziegler (2006). The Orwell accumulation in the southern North Sea (Wilkinson et al, 2009) is for example similar to the Altensalzwedel mineralogical composition. There, after millions years exposure to CO<sub>2</sub>, only minor mineral alterations were demonstrated; notably, no major dissolution of K-feldspar occurred, and likewise no detectable precipitation of dawsonite or other late carbonates was observed, contradicting expectations of geochemical modelling. This fact can be used to eliminate dawsonite from the allowed secondary minerals.

For the purpose of geochemical simulations, the representative model was scaled for a volume of one liter rock of porous medium with a porosity of 12% and a rather high initial water saturation of 30%. As possible secondary phases siderite, magnetite, chlorite and magnesite are retained. Quartz is considered inert in all simulations. The choice of secondary phases is also limited by their inclusion in the available Pitzer databases.

For such a system, the increase of CO<sub>2</sub> partial pressure to 50 bar - as an average value calculated for the injection scenarios in the Altensalzwedel reservoir - triggers the dissolution of the anhydritic cement and hematite, followed by a partial re-precipitation of calcite and siderite (figure 3). Other mineral alterations, but less important quantitatively, are the precipitation of K-feldspar and Fe-bearing illite and the dissolution of albite. Chamosite, the Fe end-member of the chlorite group, passes from oversaturated in the initial solution to undersaturated after exposure to CO<sub>2</sub>.

The first relevant observation is the negligible amount of mineral reactions predicted by the LLNL database. In this case, the increase of CO<sub>2</sub> partial pressure results in a minor dissolution of Calcite, Hematite and other silicates (not shown in figure, but always < 0.005 mol/m<sup>3</sup> rock), and precipitation of minor amounts of K-feldspar and Siderite; this results in slightly increased Al and Si concentration and decrease in Fe and K, with respect to initial fluid. Both Pitzer databases predict at the contrary an increase in the concentrations of total dissolved Fe, Al and elemental S, much larger the latter for the Quintessa's, where the most abundant aqueous sulfur species is sulfide (HS<sup>-</sup>), which is absent in GRS database. This discrepancy leads to a much larger amount of dissolved anhydrite for the Quintessa database.

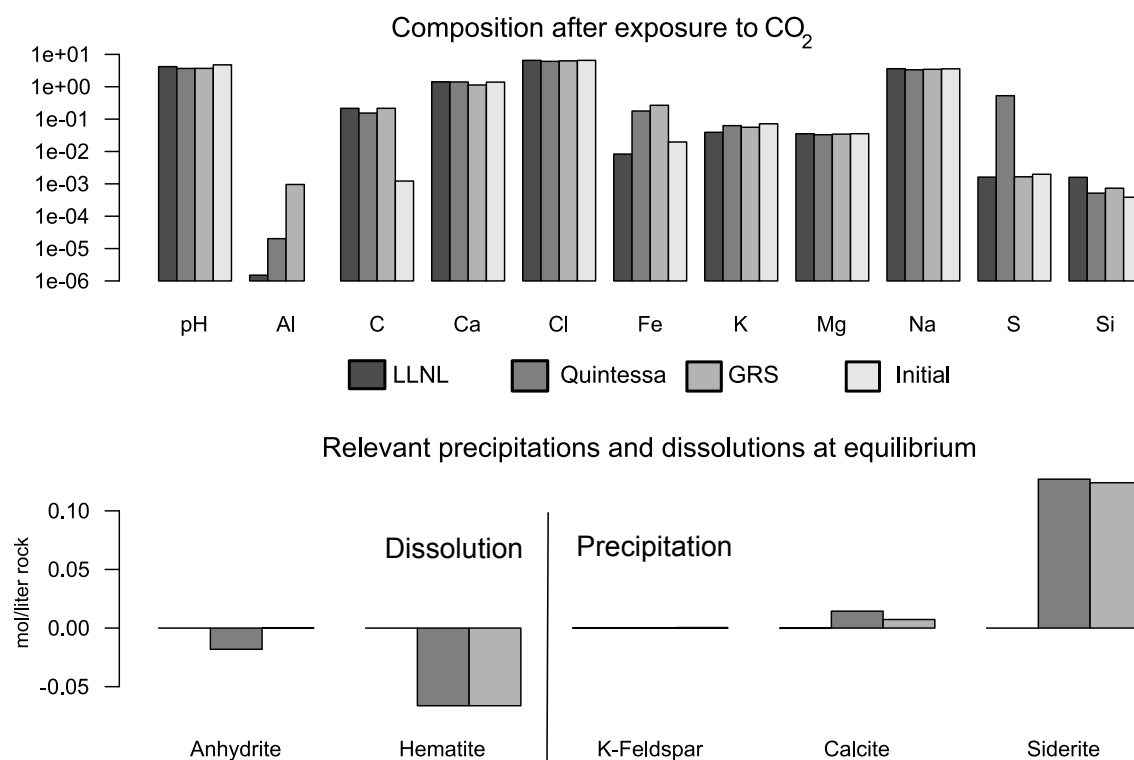


Figure 3: Predicted concentrations in mol/kgw (above) and mineral alterations in mol/L rock (below) due to injection of CO<sub>2</sub>, under the hypothesis of instantaneous equilibrium, calculated using the LLNL, Quintessa and GRS databases. The LLNL database predicts no relevant mineral reaction due to increased CO<sub>2</sub> pressure. For the two Pitzer databases, the acidification of the formation fluids triggers the dissolution of hematite and sulphate cement (anhydrite), followed by the precipitation of calcite and iron carbonates; minor quantities of K-feldspar and illite precipitate, whereas albite (not shown) is dissolved. The net volumetric effect, at equilibrium, is a moderate decrease of porosity.

Both Pitzer databases predict the decrease of dissolved K and Mg, as minor amounts of K-feldspar and illite precipitate at expenses of albite. Fe-bearing chlorite (chamosite) is strongly undersaturated after exposure to CO<sub>2</sub>, whereas it was slightly oversaturated in the fluid before exposure. The possible dissolution of chlorite in favor of illite is a well-expected fact for low pH-values (Ziegler, 2006).

These results qualitatively agree with the observations from batch experiments conducted at the University of Clausthal (Pudlo et al, this issue). Evidence of sulphate and carbonate cement dissolution were found after exposure to CO<sub>2</sub> as well as partial carbonate re-precipitation. These observations are quantitatively not comparable with the proposed model concerning the dissolution of anhydritic and carbonate cement, also because the solution used for the experiments did not contain any dissolved sulphate at the beginning. Furthermore, the precipitation of siderite, included at equilibrium in the model, is strongly kinetically controlled, likely to happen in hundreds or thousands years, therefore not observed in laboratory. However, the observations confirm that the models captured at least the direction of the most relevant expected reactions. A quantitative prediction with respect to chemical processes can only be achieved by kinetic modelling; this matter constitutes the object of the companion paper (Beyer et al, this issue) present in this issue.

The overall volumetric effect predicted by the model at equilibrium is thus a moderate loss of porosity, which can reach for this example 1.5 cm<sup>3</sup>/liter rock (less for a smaller initial water saturation), that is a reduction of around 0.15 % of porosity. This figure, though, is likely to be overestimated: the precipitation of secondary iron carbonate is kinetically slow, as already pointed out.

## 4 Conclusions and outlook

Modelling the fluid-rock interactions triggered by the injection of CO<sub>2</sub> in a deep formation is a challenging task. The thermodynamic data associated to the activity model proposed by Pitzer are patchy and incomplete and may not be valid for temperatures higher than 25 °C; but nevertheless they represent the only way to produce reasonable models for these high salinity conditions. Our study showed that simulations based on the Debye-Hückel activity model lead to severe (and systematic) discrepancies already in the simple proposed reference case where experimental data could be used for comparison.

It was possible to define a simplified geochemical model consistent with the average composition of formation fluids and the mineralogical assemblage of the host rock, however limiting the model to a restricted number of elements. The mineral phases most likely to be considered at equilibrium with the formation fluid (i.e. that are assumed to have participated in water-rock interaction in the past) are identified as albite, K-feldspar, Fe-bearing illite, calcite and anhydrite. This model was taken as representative despite the large lithological variability associated with the different layers of the reservoir and the alteration state of the sandstones. The observed variability can only be considered in the model as differential proportion of the same mineral phases, as only a limited number of minerals and reactions is defined in the thermodynamic databases within the necessary p-T range.

The simulation of reactions due to CO<sub>2</sub> injection, under the hypothesis of local thermodynamical equilibrium, results in a moderate reactivity of the system, being the dissolution of hematite and anhydrite cementation the most relevant reactions. At equilibrium, the formation of new carbonates like calcite and siderite is expected to compensate for the loss of mineral volume, with a net effect of moderate reduction of porosity (around 1.5 cm<sup>3</sup> of porous space per liter of rock are lost). Such rather small volumetric effect of mineral alteration is in line on one hand with the scarce amount of water available for reactions in the system, which is a controlling factor for chemical alterations, and on the other hand with the observations in natural analoga in similar geological settings and from laboratory experiments investigating rock material from the reservoir.

## REFERENCES

## REFERENCES

The representative model, as well as the selected Pitzer databases constitute the basis for kinetic and reactive transport simulations which will be described in the second part of this work, aiming at a quantitative assessment of the geochemical long-term effects of the injection of CO<sub>2</sub> in a depleted gas reservoir (Beyer et al, this issue).

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## References

- Accornero M, Marini L (2009): Empirical prediction of the Pitzer's interaction parameters for cationic Al species with both SiO<sub>2</sub>(aq) and CO<sub>2</sub>(aq): Implications for the geochemical modelling of very saline solutions. *Applied Geochemistry* 24(5).
- Audigane P, Lions J, Gaus I, Robelin C, Durst P, Van der Meer B, Geel K, Oldenburg C, Xu T (2009): Geochemical modeling of CO<sub>2</sub> injection into a methane gas reservoir at the K12-B field, North Sea, in M. Grobe, J. C. Pashin, and R. L. Dodge, eds, *Carbon dioxide sequestration in geological media? State of the science: AAPG Studies in Geology* 59, 499–519.
- Benbow S, Metcalfe R, Wilson J (2008): Pitzer databases for use in thermodynamic modelling. Quintessa Technical Memorandum, unpublished.
- Beyer C, Li D, De Lucia M, Kühn, M, Bauer S (2012): Modelling CO<sub>2</sub>-induced fluid-rock interactions in the Altensalzwedel gas reservoir. Part II - coupled reactive transport simulations. *Environmental Earth Sciences*, this issue. Doi:10.1007/s12665-012-1684-1.
- Christov C, Dickson A.G, Møller N (2007): Thermodynamic modeling of aqueous aluminum chemistry and solid-liquid equilibria to high solution concentration and temperature. I. the acidic H-Al-Na-K-Cl-H<sub>2</sub>O system from 0 to 100 °C. *J Solution Chem* 36(11): 1495–1523.
- Davies C (1962): *Ion association*. Butterworth, Washington D.C.
- Dethlefsen F, Haase C, Ebert M, Dahmke A (2011): Uncertainties of geochemical modeling during CO<sub>2</sub> sequestration applying batch equilibrium calculations. *Environmental Earth Sciences* 65(4): 1105–1117.
- Dick J (2008): Calculation of the relative metastabilities of proteins using the CHNOSZ software package. *Geochemical Transactions* 9:10, doi:10.1186/1467-4866-9-10.
- Duan Z, Sun R (2003): An improved model calculating CO<sub>2</sub> solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology* 193(3-4): 257–271.
- Duan Z, Sun R, Zhu C, Chou I (2006): An improved model for the calculation of CO<sub>2</sub> solubility in aqueous solutions containing Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, *Marine Chemistry*, 98 (2-4): 131–139.
- Duan Z, Møller N, Weare JH (1992): An equation of state for the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system: I. pure systems from 0 to 1000 °C and 0 to 8000 bar. *Geochimica et Cosmochimica Acta* 56: 2605–2617.

## REFERENCES

- Gailhanou H, van Miltenburg J, Rogez J, Olives J, Amouric M, Gaucher E, Blanc P (2007): Thermodynamic properties of anhydrous smectite mx-80, illite imt-2 and mixed-layer illite smectite iscz-1 as determined by calorimetric methods. part I: Heat capacities, heat contents and entropies. *Geochimica et Cosmochimica Acta* 71(22): 5463–5473.
- Gaupp R (1996): Diagenesis types and their application in diagenesis mapping. *Reviews in Mineralogy and Geochemistry* 11–12:1183–1199
- Gaus I (2010): Role and impact of CO<sub>2</sub>-rock interactions during CO<sub>2</sub> storage in sedimentary rocks (review article). *International Journal of Greenhouse Gas Control* 4(1): 73–89.
- Gaus I, Azaroual M, Czernichowski-Lauriol I (2005): Reactive transport modelling of the impact of CO<sub>2</sub> injection on the clayey cap rock at Sleipner (North Sea). *Chemical Geology* 217(3–4): 319–337.
- Gottschalk M (2007): Equations of state for complex fluids. *Reviews in Mineralogy and Geochemistry* 65: 49–97.
- Harvie C, Møller N, Weare J (1984): The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system to high ionic strengths at 25 °C. *Geochimica et Cosmochimica Acta* 48(4):723–751.
- Johnson J.W, Oelkers E, Helgeson H. (1992): SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 °C. *Comp Geosci* 19: 899–947.
- Kühn M, Förster A, Großmann J, Meyer R, Reinicke K, Schäfer D, Wendel H (2011): CLEAN: Preparing for a CO<sub>2</sub>-based enhanced gas recovery in a depleted gas field in Germany. *Energy Procedia* 4: 5520–5526.
- Kühn M, Tesmer M, Pilz P, Meyer R, Reinicke K, Förster A, Kolditz O, Schäfer D, Partners C (2012): CLEAN: CO<sub>2</sub> large-scale enhanced gas recovery in the Altmark natural gas field (Germany): Project overview. *Environmental Earth Sciences*, this issue.
- Lüders V, Plessen B, Romer R, Weise S, Banks D, Hoth P, Dulski P, Schettler G (2010): Chemistry and isotopic composition of Rotliegend and Upper Carboniferous formation waters from the North German Basin. *Chemical Geology* 276: 198–208.
- Marini L (2007): Geological sequestration of Carbon dioxide - thermodynamics, kinetics and reaction path modelling, Elsevier.
- Merkel B, Planer-Friedrich B, Nordstrom D (2005): *Groundwater Geochemistry*. Springer-Verlag,
- Moog H, Mönig H (2010): Erstellung von Parameterdateien für die Verwendung mit Chemapp und Phreeqc (BGR project 45-4500046190). Tech. rep, GRS, Braunschweig, Germany.
- Parkhurst D, Appelo C (1999): Users guide to Phreeqc (version 2). Tech. rep, U.S. Geological Survey.
- Peterson S, Hack K. (2007): The thermochemistry library Chemapp and its applications. *International Journal of Materials Research* 98:268–277.
- Pitzer K (1973): Thermodynamics of electrolytes. I. theoretical basis and general equations. *The Journal of Physical Chemistry* 77(2): 268–277.
- Pudlo D, Reitenbach V, Albrecht D, Ganzer L, Gernert U, Wienand J, Kohlhepp B, Gaupp R (2012): The impact of diagenetic fluid-rock reactions on Rotliegend sandstone composition and petrophysical properties (Altmark area, Central Germany). *Environmental Earth Sciences*, this issue.



## REFERENCES

## REFERENCES

- Regnault O, Lagneau V, Schneider H. (2009): Experimental measurement of portlandite carbonation kinetics with supercritical CO<sub>2</sub>. *Chemical Geology* 265:113–121.
- Rempel K, Liebscher A, Heinrich W, Schettler G (2011): An experimental investigation of trace element dissolution in carbon dioxide: Applications to the geological storage of CO<sub>2</sub>. *Chemical Geology* 289(3–4):224–234.
- Rumpf B, Nicolaisen H, Ocal C, Maurer G (1994): Solubility of carbon dioxide in aqueous solutions of sodium chloride: experimental results and correlation. *J Sol Chem* 23:431–448.
- Spycher N, Pruess K, Ennis-King J (2003): CO<sub>2</sub>-H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. I - assessment and calculation of mutual solubilities from 12 to 100 °C and up to 600 bar. *Geochimica et Cosmochimica Acta* 67:3015–3031.
- Spycher N, Pruess K. (2005): CO<sub>2</sub>-H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. II - partitioning in chloride brines at 12–100 °C and up to 600 bar. *Geochimica et Cosmochimica Acta* 69: 3309–3320.
- Truesdell A, Jones B (1974): Wateq, a computer program for calculating chemical equilibria of natural waters. *Journal of Research* 2:233–274.
- Wigand M, Carey JW, Schütt H, Spangenberg E, Erzinger J (2008): Geochemical effects of CO<sub>2</sub> sequestration in sandstones under simulated in situ conditions of deep saline aquifers, *Applied Geochemistry* 23, 2735–2745.
- Wilkinson M, Haszeldine R, Fallick A, Odling N, Stoker S, Gatliff R (2009): CO<sub>2</sub>-mineral reaction in a natural analogue for CO<sub>2</sub> storage-implications for modeling. *Journal of Sedimentary Research* 79:486–494.
- Wolery T (1992): Eq3/6, a software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7.0) ucrl-ma-110662. Tech. rep, Lawrence Livermore National Laboratory, Livermore, CA, USA.
- Zhang G, Spycher N, Sonnenthal E, Steefel C, Xu T (2008): Modeling reactive multiphase flow and transport of concentrated aqueous solutions. *Nuclear Technology* 164, 180–195.
- Ziegler K (2006): Clay minerals of the permian Rotliegend group in the North Sea and adjacent areas. *Clay Minerals* 41: 355–393.
- Xu T, Sonnenthal EL, Spycher N, Pruess K (2006): TOUGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media. *Computers & Geosciences* 32, 145–165.
- Xu T, Spycher N, Sonnenthal EL, Zhang G, Zheng L, Pruess K (2011): TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions, *Computers & Geosciences* 37, 763–774.