



Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

IChemE

Comparison of numerical codes for geochemical modelling of CO₂ storage in target sandstone reservoirs

Ozgur Gundogan*, Eric Mackay, Adrian Todd

Institute of Petroleum Engineering, Heriot-Watt University, EH14 4AS, Edinburgh, UK

ABSTRACT

Long-term containment of CO₂ and storage security depends mainly on physical and geochemical trapping mechanisms. Injected CO₂ dissolves in the formation fluid and causes a sharp decrease in pH which in turn drives the dissolution and precipitation of minerals. Geochemical modelling is an important tool to understand and predict the behaviour of CO₂ reactivity. In this paper three numerical codes, PHREEQC, GEM and TOUGHREACT, are compared with respect to brine – CO₂ – rock reactions. Formation water compositions and mineralogies of three sandstone core samples from target CO₂-storage formations were used as input for kinetic models. Mineral replacement reactions were observed when CO₂ injection was initiated in all scenarios. While PHREEQC and GEM were generally in good agreement, TOUGHREACT gave diverging predictions on two models. It is considered that the discrepancies are caused primarily by the differences in the thermodynamic databases and activity models. The uncertainties in these calculations suggest that appropriate experimental tests should be performed to validate the models, so that they can be used to make predictions at the field scale.

© 2010 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: CO₂ sequestration; Chemical reactions; Dissolution; Precipitation; Geochemical simulation; North Sea

1. Introduction

While the international scientific and political community debates the relative uncertainties of climate change, the reduction of anthropogenic CO₂ emissions is taken as a precautionary measure. The Intergovernmental Panel on Climate Change (IPCC, 2005) considers carbon dioxide capture and geological storage (CCS) in the portfolio of mitigation options for stabilizing atmospheric greenhouse gases. In 2009 the European Council adopted a directive to enable environmentally safe CCS (2009/31/EC). The directive outlines the regulatory framework for the commission, member states and potential CCS operators. It specifies the characterisation and assessment criteria to determine the suitability of a geological formation for use as a storage site. According to these criteria, characterisation of the dynamic storage behaviour requires, among other things, consideration of the reactive processes and development of an insight into changes in formation fluid chemistry and subsequent reactions, and use of reactive modelling to assess these processes.

The major concerns for reactive processes are long-term containment of CO₂ and maintenance of injectivity. This is because when CO₂ dissolves in the formation fluid the pH of the solution decreases and this can drive mineral dissolution and there may be subsequent precipitation involving the dissolved salts. Computer codes such as PHREEQC, GEM and TOUGHREACT are widely used to simulate these reactive processes (Gaus et al., 2005; Audigane et al., 2007; Wigand et al., 2008; Xu et al., 2005; Thibeau et al., 2007; Cantucci et al., 2009). In this paper these simulators are compared with respect to brine – CO₂ – rock reactions in potential target sandstone formations in the North Sea.

2. Model setup

2.1. Description of the reservoirs

Reservoirs suitable for CO₂ storage have good porosity and permeability which allows injected CO₂ to displace the fluid in the host rock and occupies the pore space. In addition the reser-

* Corresponding author. Tel.: +44 131 451 4316; fax: +44 131 451 3127.

E-mail addresses: ozgur.gundogan@pet.hw.ac.uk, ozgur@libero.it (O. Gundogan), eric.mackay@pet.hw.ac.uk (E. Mackay), adrian.todd@pet.hw.ac.uk (A. Todd).

Received 25 May 2010; Received in revised form 1 September 2010; Accepted 10 September 2010

0263-8762/\$ – see front matter © 2010 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

doi:10.1016/j.cherd.2010.09.008

Nomenclature

a	activity
A	temperature dependent coefficient in activity models
\bar{a}_i	ion size parameter of species i
A_β	reactive surface area of mineral β
B	temperature dependent coefficient in activity models
b	temperature dependent coefficient in activity models
$b_{\text{Na}^+, \text{Cl}^-}$	Debye–Hückel parameter
b_{NaCl}	Debye–Hückel parameter
E_a	activation energy
$f_{\text{CO}_2(\text{aq})}$	fugacity of CO_2 in the aqueous phase
$f_{\text{CO}_2(\text{g})}$	fugacity of CO_2 in the gas phase
H	Henry's constant
I	ionic strength of the solution
k_{25}	rate constant at 25 °C
K_T	chemical equilibrium constant at temperature T
K_β	chemical equilibrium constant
k_β	rate constant
m	molality
m^*	total molality
P_{CO_2}	partial pressure of CO_2
Q_β	ionic activity product
R	universal gas constant
r_β	dissolution/precipitation rate for mineral β
T	temperature
y_{CO_2}	molar fraction of CO_2 in the aqueous phase
z_i	ionic charge of species i
γ	activity coefficient
γ_i	activity coefficient of species i
ω_i	Born coefficient
Φ	fugacity coefficient

voirs also have caprock that prevents the escape of CO_2 , and high enough pressure and temperature that the stored CO_2 will be in the supercritical state, which maximizes the storage capacity. Rannoch, Oseberg and Forties formations of the northern part of the North Sea are candidate formations for CO_2 storage. Three core samples were taken from these formations and analyses were performed to identify the mineralogy of these cores, and the composition of the formation water, although CO_2 injection was not performed.

Modelling was performed at reservoir temperature and at an estimated maximum allowable pressure during injection (Table 1). The fugacity of CO_2 is calculated under these conditions with the Duan and Sun model (2003), and is given together with reservoir parameters in Table 1.

Table 1 – Physical properties of the reservoirs.

	Rannoch	Oseberg	Forties
Temperature (°C)	92	100	96
Pressure (bar)	460	280	172
Fugacity of CO_2 (bar) (calculated)	201.71	151.20	110.80
Porosity (%)	25	20	22
k (mD)	200	600	700

2.2. Simulation codes

The three codes used in this paper are briefly summarised below. More detailed information on the codes can be found in the cited references.

PHREEQC v.2.15 (Parkhurst and Appelo, 1999) is mainly a general purpose geochemical code, including the capability to simulate monophasic 1D reactive transport. A feature of PHREEQC is its ability to be adapted to specific geochemical problems by modifying its database (reactions and species can be added or suppressed easily) and/or adding specific modules (programmed in BASIC) to take into account, for instance, a particular kinetic law. Coupling between chemistry and transport is based on the operator splitting technique (advective, dispersive and reaction operators are split) with a specific sequential iterative algorithm. PHREEQC uses the law of mass action approach. PHREEQC may be used in batch mode or as a one dimension discretised linear transport model.

GEM v.2009.13 (Nghiem et al., 2004) is a fully coupled geochemical compositional equation of state simulator for modelling CO_2 and acid gas enhanced oil recovery (EOR) and storage processes. GEM uses a one step approach and can model convective and dispersive flow; phase equilibrium between oil, gas and brine; chemical equilibrium reactions among aqueous components; and mineral dissolution and precipitation kinetics. The simulator uses an adaptive implicit discretisation technique to model the component transport in porous media in one, two or three dimensions. The oil and gas phases are modelled with an equation of state, and the gas solubility in the aqueous phase is modelled with Henry's law. Vaporization of H_2O into the gas phase, thermal effects and leakage through cap rock, and sealing faults also are modelled. GEM also uses the law of mass action approach.

TOUGHREACT v.1.21 (Xu et al., 2006) is a non-isothermal reactive transport code. It was developed by introducing reactive chemistry into the framework of the existing multi phase fluid and heat code TOUGH2. It uses a sequential iterative approach. TOUGHREACT can be used for batch geochemical modelling and to model reactive transport in one, two and three dimensions. The model can include any number of chemical species in liquid, gas and solid phases. Aqueous chemical complexation and gas dissolution/exsolution are considered under the local equilibrium assumption. Mineral dissolution/precipitation can proceed either subject to local equilibrium or kinetic conditions with coupling to changes in porosity with permeability, and capillary pressure in under-saturated systems. TOUGHREACT uses the ECO2N module, which is a fluid property module for the TOUGH2 simulator (Version 2.0) that was designed for applications to geologic sequestration of CO_2 in saline aquifers. It includes a comprehensive description of the thermodynamics and thermophysical properties of H_2O – NaCl – CO_2 mixtures, which reproduces fluid properties largely within experimental error for the temperature, pressure and salinity conditions of interest ($10^\circ\text{C} \leq T \leq 110^\circ\text{C}$; $P \leq 600$ bar; salinity up to halite saturation) (Pruess and Spycher, 2007).

2.3. Modelling approach

As the objective of the paper is to compare the geochemical calculations of the codes, in order to simplify the problem, the transport effects are not considered. The easiest way to compare geochemical simulations is by batch modelling. While batch modelling is straightforward in PHREEQC

Table 2 – Mineralogical composition of the samples used in this study.

Mineral	Rannoch		Oseberg		Forties		Chemical formula
	Vol. fr. (%)	mol/m ³ rock	Vol. fr. (%)	mol/m ³ rock	Vol. fr. (%)	mol/m ³ rock	
Calcite	0.0	0	1.0	271	2.0	542	CaCO ₃
Chalcedony	62.5	27,548	62.0	27,327	55.0	24,242	SiO ₂
Clinochlore	1.5	72	–	–	–	–	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈
Dolomite-dis	0.0	0	0.0	0	1.0	155	CaMg(CO ₃) ₂
K-feldspar	5.0	459	5.0	459	6.0	551	KAlSi ₃ O ₈
Illite	–	–	1.0	72	–	–	K _{0.6} Mg _{0.25} Al _{1.8} Al _{10.5} Si _{3.5} O ₁₀ (OH) ₂
Kaolinite	–	–	4.0	402	2.0	201	Al ₂ Si ₂ O ₅ (OH) ₄
Magnesite	0.0	0	0.0	0	–	–	MgCO ₃
Muscovite	4.0	284	0.0	0	0.0	0	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂
Siderite	–	–	–	–	5.0	1746	FeCO ₃

and TOUGHREACT, it is not possible in GEM. In GEM a one-dimensional homogeneous model was used instead. A system was modelled with a constant CO₂ pressure, which supplies abundant CO₂ to the aqueous system throughout the simulations. This system represents more closely the top of the reservoir with a CO₂ cap.

2.4. The baseline geochemical conditions

It is necessary to define the initial geochemical conditions of the reservoir prior to CO₂ injection. This requires the need to assess the mineralogy and fluid composition of the reservoir. In this paper the data from the core and fluid samples of candidate sandstone reservoirs from the North Sea are used.

2.4.1. Initial mineralogy

The mineralogy of the core samples was taken from the petrographic analysis data. In some cases these analyses were not specific enough and it was necessary to select some minerals as proxies. Muscovite was a proxy for mica, and clinochlore-14A was a proxy for chlorite. Feldspars were predominantly K-feldspar and modelled as K-feldspar. Chalcedony was used instead of quartz because natural waters at low temperature are usually oversaturated with respect to quartz, which also is the case in the North Sea reservoirs (Bazin et al., 1997; Gaus et al., 2005). The minerals containing less than 1% of the overall bulk volume fraction were not modelled. The mineralogical compositions used in the modelling are given in Table 2.

2.4.2. Initial brine composition

The thermodynamic equilibrium of the formation water with the mineralogy of the reservoir is assumed as the initial reference state for the fluid composition. Hence the formation water samples were equilibrated with the minerals of the core samples defined above by using PHREEQC. This simulated brine composition was used as the initial brine in the modelling of the CO₂ reactions in the cores.

Before the equilibration with minerals, the water samples were analyzed to check the quality of the samples and the consistency with the thermodynamic data. The analytical data and the equilibrium model are in good agreement. Because the concentration of Cl[–] was determined by the charge balance there are slight differences in the Cl concentration. As can be seen from Table 3, equilibration of the brine with the mineralogy of the cores caused changes in the pH and composition. This is because minerals dissolved or precipitated in order to reach equilibrium.

2.4.3. Secondary minerals

Secondary minerals are the ones that are not present initially but can be formed during the simulations. The secondary minerals were selected by evaluating their degree of saturation in the CO₂ saturated brine model using PHREEQC. The minerals that are supersaturated and can likely precipitate under reservoir conditions were selected as secondary minerals. One exception to this is the iron minerals other than siderite, since we did not model them. The secondary minerals are denoted with zero initial volume fractions in Table 2.

3. Comparison of results

3.1. Thermodynamic equilibrium modelling

One of the fundamental requirements of geochemical modelling is the calculation of the species in the aqueous phase. The main assumption is local thermodynamic equilibrium as the aqueous phase is dominated by fast reactions. To study a reaction we need to write the mass action equation that relates the activities of the species to the reaction's equilibrium constant. At equilibrium the ion activity product is equal to the equilibrium constant. The internal databases of GEM and TOUGHREACT and the Lawrence Livermore National Laboratory (LLNL) database of PHREEQC for thermodynamic data were used. The equilibrium constants are reported at 25 °C in the databases, and these were extrapolated to the reservoir temperatures. The codes use the following equations to derive equilibrium constants at T in °C for GEM and in K for others:

$$\text{PHREEQC: } \log K_T = a + bT + \frac{c}{T} + d \log T + \frac{e}{T^2}$$

$$\text{TOUGHREACT: } \log K_T = a \ln T + b + cT + \frac{d}{T} + \frac{e}{T^2}$$

$$\text{GEM: } \log K_T = a + bT + cT^2 + dT^3 + eT^4$$

where K_T is the equilibrium constant at temperature T , a , b , c , d , e are the constants.

Note that all three codes neglect the effect of pressure on the equilibrium constants, although the impact of pressure can be significant at high pressures.

Because speciation and mineral precipitation and dissolution calculations are based on mass action equations, activity models are crucial for the accuracy of these calculations. Activity models also are important for mineral precipitation or dissolution reactions. Because precipitation occurs when a solution becomes oversaturated with respect to a solid phase,

Table 3 – The composition of the initial brine sample data, the modelled initial brine and the initial brine after equilibration with mineralogy.

	Oseberg			Rannoch			Forties		
	Sample	Model	Eq. model	Sample	Model	Eq. model	Sample	Model	Eq. model
T (°C)	100	100	100	92	92	92	96	96	96
pH	6.04	6.04	6.04	6.90	6.90	6.34	7.00	7.00	5.77
Ionic strength	–	0.66	0.66	–	0.54	0.54	–	1.37	1.36
Composition (mol/kg H ₂ O)									
Al	–	–	1.32E–07	–	–	7.27E–08	–	–	6.86E–08
Ca	2.20E–02	2.20E–02	2.15E–02	9.00E–03	9.00E–03	9.00E–03	7.00E–02	7.00E–02	6.22E–02
Cl	6.75E–01	6.80E–01	6.80E–01	5.50E–01	5.60E–01	5.60E–01	1.48E+00	1.46E+00	1.46E+00
Fe	–	–	–	–	–	–	1.65E–04	1.65E–04	5.25E–04
K	1.30E–02	1.30E–02	3.95E–03	1.40E–02	1.40E–02	4.20E–03	1.00E–02	1.00E–02	7.98E–03
Mg	5.00E–03	5.00E–03	9.90E–03	2.00E–03	2.00E–03	6.30E–03	2.10E–02	2.10E–02	2.69E–02
Na	6.16E–01	6.16E–01	6.16E–01	5.29E–01	5.29E–01	5.29E–01	1.28E+00	1.28E+00	1.28E+00
Si	–	–	1.45E–03	–	–	1.25E–03	–	–	1.35E–03

activity models are essential when the degree of saturation with respect to a solid is calculated.

The activity of a species depends on the pressure, temperature and the solution composition. An activity correction is needed to take into account the non-ideality of the solution.

Activity is related to molality as follows:

$$a = \gamma m \quad (1)$$

where a is the activity, γ is the activity coefficient and m is the molality of the species.

Activity corrections are based on the Debye–Hückel or the B-dot model for GEM. PHREEQC uses the B-dot model as default for the LLNL database but the Davies equation can also be used with modification of the database. In this study the B-dot model (Helgeson, 1969) is used in both GEM and PHREEQC.

In the B-dot model the activity of an ion is computed by

$$\log \gamma_i = - \left(\frac{A z_i^2 I^{1/2}}{1 + \hat{a}_i B I^{1/2}} \right) + b I \quad (2)$$

where γ_i , \hat{a}_i , z_i are the activity coefficient, the ion size parameter, and the ionic charge of the species i , A , B and b are temperature dependent coefficients and I is the ionic strength of the solution.

For uncharged species, the first term of Eq. (2) becomes zero and the B-dot equation reduces to the Setchenow equation:

$$\log \gamma_i = b I \quad (3)$$

PHREEQC calculates the activity coefficient of uncharged species specified with “-CO2-llnl-gamma” (essentially the nonpolar neutral species) with the following equation derived by Drummond (Wolery, 1992):

$$\ln \gamma_i = \left(a + bT + \frac{c}{T} \right) I - (d + eT) \left(\frac{I}{I+1} \right) \quad (4)$$

where T is the absolute temperature, a , b , c , d , e , are the constants and I is the ionic strength. The activities of the other uncharged species are assumed to be one.

In GEM, the activities of uncharged species are set to one.

TOUGHREACT uses the extended Debye–Hückel equation from Helgeson, Kirkham, and Flowers (Helgeson et al., 1981) to compute the activity coefficients of charged species and

water:

$$\log \gamma_i = - \left(\frac{A z_i^2 I^{1/2}}{1 + \hat{a}_i B I^{1/2}} \right) + \log(1 + 0.0180153 m^*) - (\omega_i b_{\text{NaCl}} + b_{\text{Na}^+, \text{Cl}^-} - 0.19(|z_i| - 1)) I \quad (5)$$

where γ_i , \hat{a}_i , z_i are the activity coefficient, the ion size parameter, and the ionic charge of the species i , A and B are temperature dependent coefficients, m^* is the total molality, I is the ionic strength of the solution, ω_i is the Born coefficient, b_{NaCl} and $b_{\text{Na}^+, \text{Cl}^-}$ are Debye–Hückel parameters.

The activity of dissolved gases (CO₂(aq), CH₄(aq), H₂(aq), H₂S(aq), O₂(aq), SO₂(aq)) are calculated by Eq. (4). For all the other uncharged species, activity coefficients are assumed to be one by default or can be computed by Eq. (3).

All these models are valid for salinities below 1M where the influence of the medium is calculated as a whole by ionic strength. For higher salinities it is necessary to take into account the influence of each specific species by using the Pitzer formalism. Only PHREEQC has a Pitzer database for more concentrated solutions, but this database does not include all the minerals used in this study.

The equilibrium constants used by the codes are compared in Table 4. There is good agreement between the logK values for chalcedony, clinocllore-14A, and carbonates except siderite at 100 °C. On the other hand there are significant differences between the logK values of other minerals.

3.2. Solubility of CO₂

An accurate calculation of the solubility of CO₂ is essential not only for the storage capacity estimation of the aquifer but also for the fluid–rock interactions. The solubility of the CO₂ depends on pressure, temperature, and salinity.

The dissolution of CO₂ can be expressed as the chemical reaction:



where CO₂(g) is the CO₂ in the gas phase and CO₂(aq) is the CO₂ in the aqueous phase. Because this reaction is fast, thermodynamic equilibrium is assumed between the phases.

Thermodynamic equilibrium is the equality of the fugacities of the components in the gas and aqueous phases (Nghiem et al., 2004).

Table 4 – Comparison of the equilibrium constants for the minerals used in this study.

Minerals	log K at 25 °C			log K at 100 °C		
	PHREEQC	GEM	TOUGHREACT	PHREEQC	GEM	TOUGHREACT
Calcite	Calcite + H ⁺ = Ca ²⁺ + HCO ₃ [−] 1.82	1.71	2.15	0.79	0.69	0.77
Chalcedony	Chalcedony = SiO ₂ (aq) −3.76	−3.74	−4.19	−2.84	−2.87	−2.86
Clinocllore-14A	Clinocllore-14A + 16 H ⁺ = 12 H ₂ O + 5 Mg ²⁺ + 2 Al ³⁺ + 3 SiO ₂ (aq) 67.05	68.58	72.75	45.27	47.28	44.24
Dolomite	Dolomite-dis + 2 H ⁺ = Ca ²⁺ + Mg ²⁺ + 2 HCO ₃ [−] 2.47	4.06	4.93	1.24	1.24	1.20
Illite	Illite + 8 H ⁺ = 5 H ₂ O + 0.6 K ⁺ + 0.25 Mg ²⁺ + 2.3 Al ³⁺ + 3.5 SiO ₂ (aq) 8.88	9.80	7.27	2.15	3.76	−0.97
Kaolinite	Kaolinite + 6 H ⁺ = 5 H ₂ O + 2 Al ³⁺ + 2 SiO ₂ (aq) 6.72	7.43	7.96	1.02	2.40	−0.09
K-feldspar	K-feldspar + 4 H ⁺ = 2 H ₂ O + K ⁺ + Al ³⁺ + 3 SiO ₂ (aq) −0.38	0.07	0.72	−1.78	−1.10	−1.94
Magnesite	Magnesite + H ⁺ = Mg ²⁺ + HCO ₃ [−] 2.27	2.44	2.83	0.61	0.71	0.58
Muscovite	Muscovite + 10 H ⁺ = 6 H ₂ O + K ⁺ + 3 Al ³⁺ + 3 SiO ₂ (aq) 13.45	14.57	16.42	4.3	6.41	4.19
Siderite	Siderite + H ⁺ = HCO ₃ [−] + Fe ²⁺ −0.22	−0.22	9.89	−1.48	−1.51	3.43

The fugacity of CO₂ in the gas phase is defined as

$$f_{\text{CO}_2(\text{g})} = P_{\text{CO}_2} \Phi \quad (7)$$

where $f_{\text{CO}_2(\text{g})}$ is the fugacity of CO₂ in the gas phase, P_{CO_2} is the partial pressure of CO₂ and Φ is the fugacity coefficient.

On the other hand the fugacity of CO₂ in the aqueous phase is defined as

$$f_{\text{CO}_2(\text{aq})} = y_{\text{CO}_2} H \quad (8)$$

where $f_{\text{CO}_2(\text{aq})}$, y_{CO_2} are the fugacity and the molar fraction of CO₂ in the aqueous phase and H is Henry's constant.

From Eqs. (7) and (8) the mole fraction of CO₂ in the aqueous phase is derived:

$$y_{\text{CO}_2} = \frac{P_{\text{CO}_2} \Phi}{H} \quad (9)$$

GEM and TOUGHREACT use corrected Henry's constants in order to take account of pressure and salinity effects. PHREEQC does not use fugacity coefficient and assumes that the fugacity of a gas is equal to its partial pressure. This overestimates the solubility at high pressures. The CO₂ fugacities calculated with [Duan and Sun model \(2003\)](#) were used for PHREEQC calculations. As shown in [Table 5](#), the correction of fugacity reduces the overestimation but there are still significant discrepancies. This is because PHREEQC does not consider the effect of pressure on the equilibrium constants. On the other hand, TOUGHREACT overestimated the CO₂ solubility in the Rannoch model, which is the one with the highest fugacity of the three cases.

3.3. pH

The decrease of the pH in the formation fluid with CO₂ injection is observed both in laboratory and field tests ([Kaszuba et](#)

Table 5 – Computed CO₂ solubility in different models (PHREEQC_gas is the PHREEQC model without fugacity correction, PHREEQC is the PHREEQC model with fugacity correction).

Sample	CO ₂ (aq) (M)					
	f_{CO_2} (bar)	Reference model	PHREEQC_gas	PHREEQC	GEM	TOUGHREACT
Rannoch	201.71	1.31	4.59	2.01	1.35	1.98
Oseberg	151.20	1.11	2.56	1.39	1.13	1.19
Forties	110.80	0.82	1.44	0.93	0.83	0.76

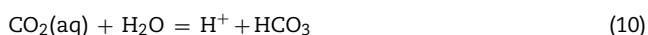
Table 6 – The equilibrium constants of the dissociation reactions (10) and (11).

	log K at 25 °C			log K at 100 °C		
	PHREEQC	GEM	TOUGHREACT	PHREEQC	GEM	TOUGHREACT
CO ₂ (aq)	−6.37	−6.38	−6.52	−6.37	−6.43	−6.39
HCO ₃ [−]	−10.35	−10.35	−10.55	−10.07	−10.24	−10.09

Table 7 – pH values of the initial CO₂ saturated brine and final brine.

Sample	PHREEQC		GEM		TOUGHREACT	
	Initial brine	Final brine	Initial brine	Final brine	Initial brine	Final brine
Rannoch	3.39	5.14	3.63	5.03	3.53	4.87
Oseberg	3.41	4.90	3.60	5.00	3.58	5.01
Forties	3.46	4.77	3.65	4.88	3.59	4.87

al., 2005; Kharaka et al., 2006). Dissolved CO₂ forms a weak acid in the solution which can be expressed by the following chemical reactions:



The equilibrium constants of these reactions are given in Table 6.

A sharp decrease of the pH was observed in all the three samples. Later, due to the mineral reactions, the pH started to increase. Because of the fast dissolution kinetics of calcite, the pH of the brine increased, in just 1000 s, to 4.45 in the Oseberg rock type and to 4.51 in the Forties rock type and reached the final values by buffering of silicate minerals. On the other hand, as calcite is absent in the Rannoch sample, pH increased slowly throughout the simulation. The simulators are in reasonably good agreement, as seen from Table 7.

3.4. Mineral dissolution and precipitation

When a mineral comes into contact with CO₂ saturated brine which was not in equilibrium previously, the mineral starts to dissolve in order to reach equilibrium with the brine. The dissolution of the mineral changes the brine composition and can drive the precipitation of secondary minerals. For example, if K-feldspar comes into contact with CO₂ saturated brine, it dissolves. The release of Al, Si and K ions enriches the brine, and it becomes supersaturated with respect to muscovite. If it is sufficiently supersaturated for nucleation, muscovite precipitates.

In thermodynamic equilibrium models supersaturation of a mineral is not allowed. On the other hand, whether or not a mineral actually precipitates depends on the kinetic rate of the reaction. Therefore the kinetics reaction modelling allows the supersaturation of the mineral phases in the solution. For this reason a kinetic law was used for the dissolution and precipitation of minerals. The reaction rate depends on the how much of the mineral is available, how fast the reaction is and how far it is from the equilibrium.

A simplified kinetics rate law (Steefel and Lasaga, 1994) was considered:

$$r_\beta = k_\beta A_\beta \left(1 - \frac{Q_\beta}{K_\beta}\right) \quad (12)$$

where r_β is the dissolution/precipitation rate for mineral β per unit bulk volume of porous medium or per volume of aqueous phase [$\text{mol m}^{-3} \text{s}^{-1}$], A_β is the reactive surface area of mineral β [m^2], k_β is the rate constant [$\text{mol m}^{-2} \text{s}^{-1}$], K_β is the chemical equilibrium constant, and Q_β is the ionic activity product.

In the simulations A is expressed as per unit of rock volume in GEM and TOUGHREACT, whereas it is expressed as per mole in PHREEQC, so it is updated by the simulator with volume

Table 8 – Reaction rate constants and activation energies for minerals used in the simulations.

Mineral	k (25 °C)	EA (kJ)
Calcite	1.50E–06	41.9
Chalcedony	3.45E–13	62.8
Clinochlore	3.00E–13	88.0
Dolomite-dis	1.00E–09	62.8
K-feldspar	1.78E–10	51.7
Illite	1.00E–13	22.0
Kaolinite	4.00E–13	29.0
Magnesite	1.00E–09	62.8
Muscovite	1.00E–13	22.0
Siderite	1.00E–09	62.8

change and mole change, respectively. Reactive surface areas are case specific and they need to be measured case by case. Because measurements of BET surfaces were not available, a universal value of $10^4 \text{ m}^2 \text{ per m}^3$ of rock was assumed, except that for the phyllosilicates. Because of the fine grain size of phyllosilicates, the surface area for these minerals was set to $10^6 \text{ m}^2 \text{ per m}^3$. To allow the precipitation of the secondary minerals, their volume fraction was set to 10^{-6} to 10^{-7} so that their reactive surfaces were non-zero.

The Arrhenius equation can be used to describe the temperature dependence of the rate constant. The rate constants are reported usually at 25 °C this is expressed as (Steefel and Lasaga, 1994):

$$k = k_{25} \exp \left(\frac{-E_a}{R (1/T - 1/298.15)} \right) \quad (13)$$

where k_{25} is the rate constant at 25 °C [$\text{mol m}^{-2} \text{s}^{-1}$], E_a is the activation energy [J/mol], R is the universal gas constant [$8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$], and T is the temperature [K].

The rate constants and the activation energies used in this study (Table 8) were from Johnson et al (2004 and references cited therein) with the exception of the activation energy of calcite (Svensson and Dreybrodt, 1992). The kinetic data of disordered dolomite and siderite were assumed to be equal to those of magnesite, and the kinetic data of illite to those of muscovite.

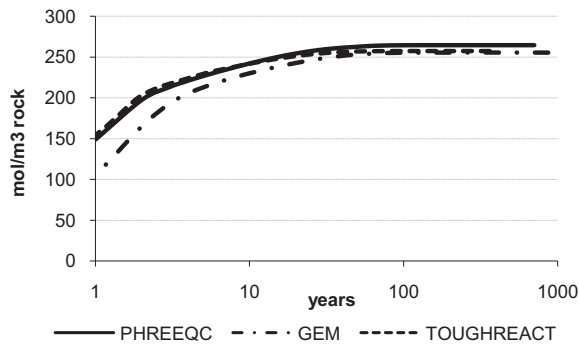
In GEM and TOUGHREACT it is necessary to specify the aqueous species that will be modelled. The following species were modelled: H^+ , Ca^{2+} , $\text{SiO}_2(\text{aq})$, K^+ , Al^{3+} , Na^+ , Cl^- , HCO_3^- , CO_3^{2-} , OH^- , Fe^{2+} , Mg^{2+} , AlOH^{2+} . On the other hand, in the PHREEQC models all the aqueous species available in the database are used for modelling.

As the kinetic data are not well known, the length of time that the reactions take should be considered as qualitative rather than quantitative.

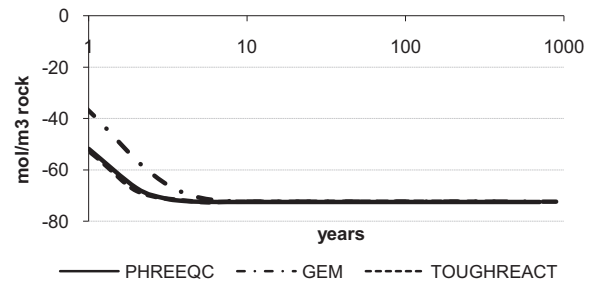
3.5. The mineral reactions observed in the simulations

In Rannoch rock type, the decrease of pH by CO₂ dissolution initiated clinocllore and K-feldspar dissolution. The dissolu-

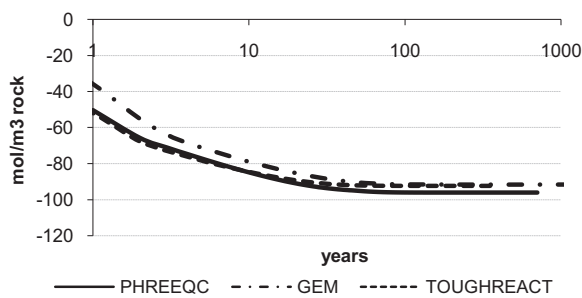
a Chalcedony



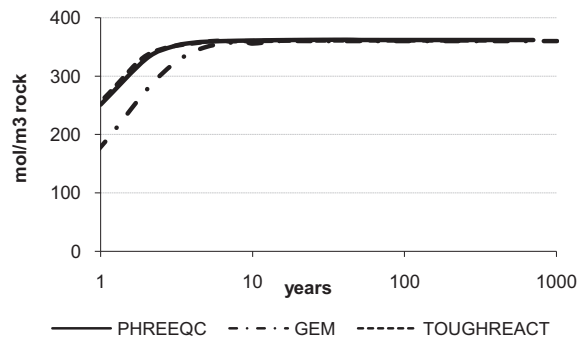
b Clinocllore



c K-feldspar



d Magnesite



e Muscovite

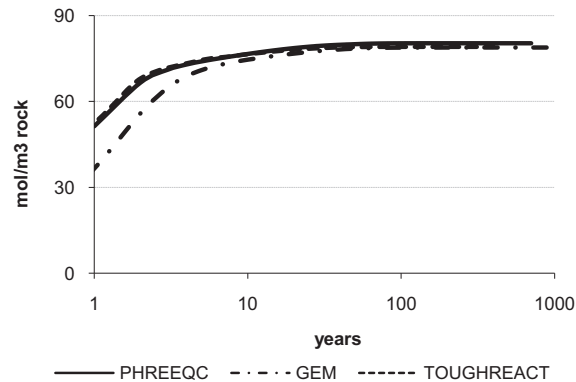
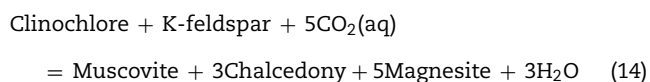


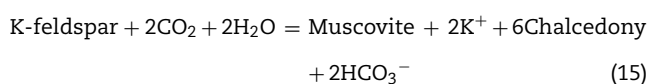
Fig. 1 – Mineral changes in moles per m³ of medium with time (positive values precipitation, negative values dissolution) for Rannoch rock type.

tion of these minerals released Mg, K, Al, and Si ions into the brine which lead to supersaturation and precipitation of magnesite, muscovite and chalcedony.

The overall reaction observed can be expressed as

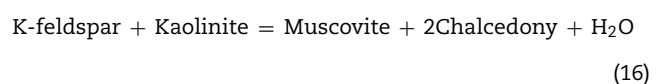


The equation shows that for each mole of clinocllore dissolved, five moles of CO₂ is trapped as magnesite. The clinocllore was consumed in less than 10 years and K-feldspar continued to dissolve until the K-feldspar—muscovite equilibrium was reached. This reaction can be written as



As can be seen from Fig. 1, the three simulators are in very good agreement for the five minerals after 10 years of simulation.

For Oseberg rock type, PHREEQC and GEM predicted, in the early time of the simulations, the dissolution of illite which enriched the brine with K, Al, and Si ions. This enrichment initiated the precipitation of kaolinite, K-feldspar and chalcedony. The kaolinite and K-feldspar formed were not stable and they started to dissolve later on. Illite also released Mg²⁺ which induced a trace amount of dolomitization. After approximately 1000 years, illite was consumed. K-feldspar and kaolinite continued to dissolve, and muscovite and chalcedony precipitated by the following overall reaction:



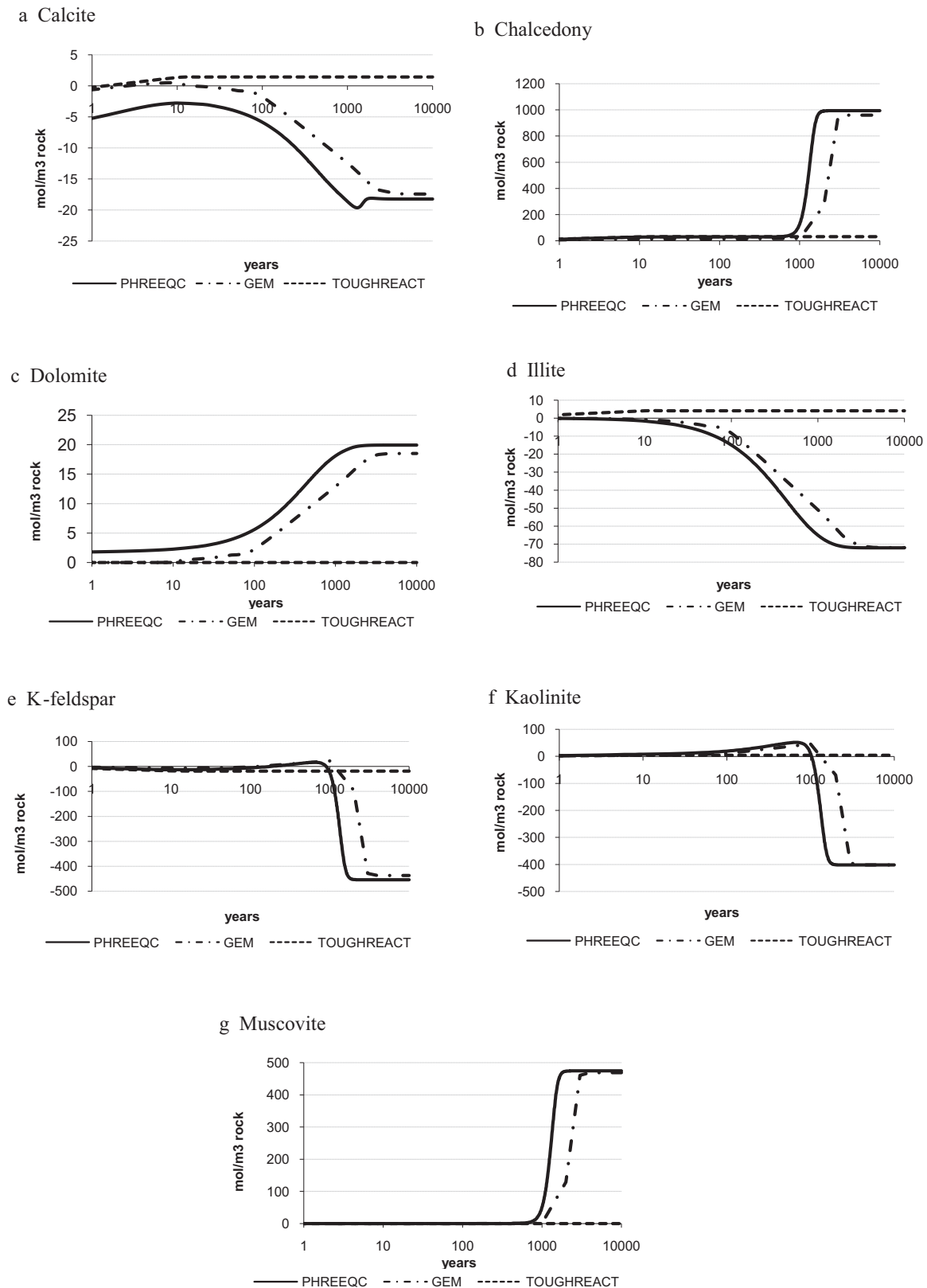


Fig. 2 – Mineral changes in moles per m³ of medium with time (positive values precipitation, negative values dissolution) for Oseberg rock type.

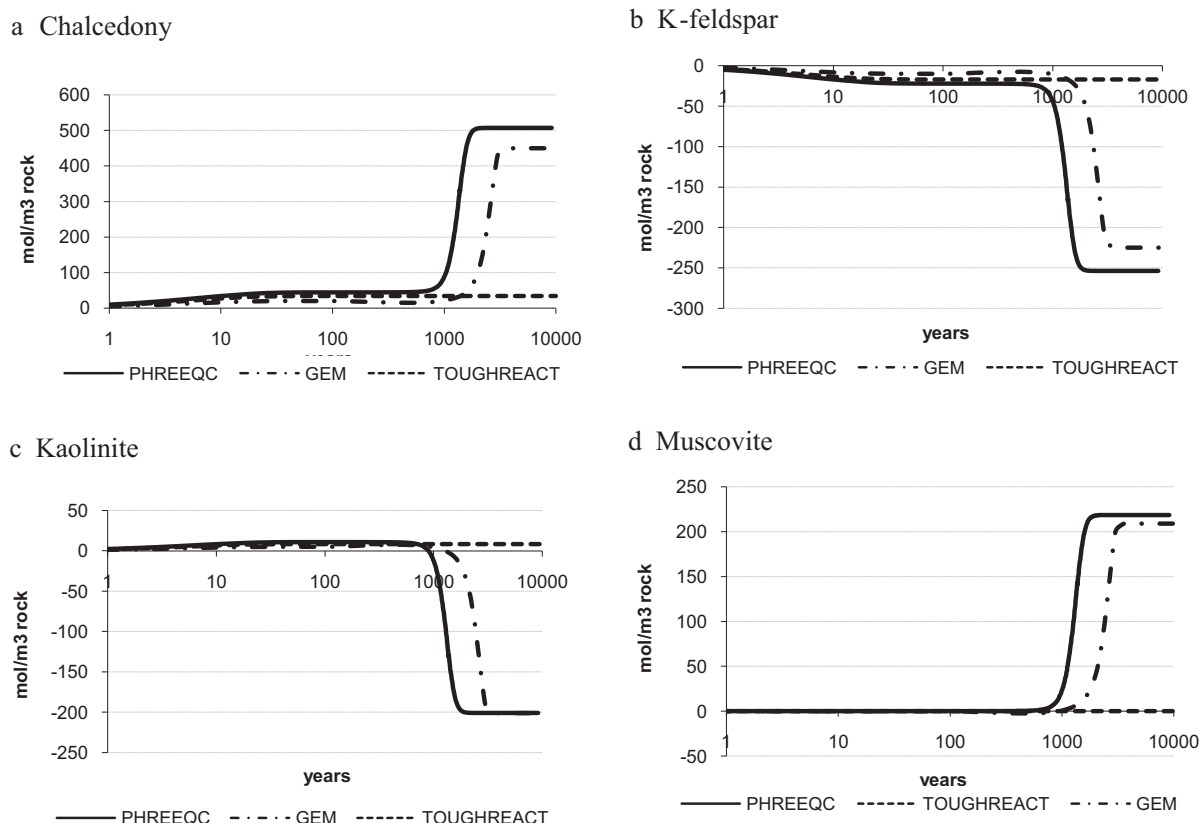
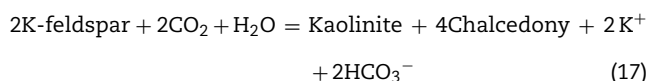


Fig. 3 – Mineral changes in moles per m³ of medium with time (positive values precipitation, negative values dissolution) for Forties rock type.

In contrast, TOUGHREACT simulated a low level of reactivity with a minor amount of illite precipitation and feldspar dissolution. The comparison of the three codes with respect to mineral changes is given in Fig. 2.

In Forties rock type, initially the K-feldspar dissolution and the kaolinite precipitation is observed by PHREEQC and GEM:



Then kaolinite started to dissolve with K-feldspar, and muscovite and chalcedony precipitated.

As in the case of Oseberg rock type, TOUGHREACT simulated a low level of reactivity with minor dissolution of feldspar, and precipitation of kaolinite and chalcedony. The comparison of the three codes with respect to mineral changes is shown in Fig. 3.

In conclusion, there is fairly good agreement between PHREEQC and GEM in all three cases, whereas TOUGHREACT gave diverging results in the Oseberg and Forties models. The major reason for the low level of reactivity in TOUGHREACT is that the simulator predicted negative saturation index for muscovite. With no muscovite precipitation, and hence no sink for K⁺, K-feldspar reached equilibrium with the brine and stopped dissolving.

In order to identify if the differences in the results are due to the differences in thermodynamic data, the simulations of the Oseberg rock type were re-run with the same thermodynamic data by using the PHREEQC's equilibrium constants for aqueous and mineral reactions in the three codes. The sim-

Table 9 – Comparison of computed activity coefficients and activities for the initial brine of Oseberg formation given in Table 3.

Species	Activity (log molal except for H ₂ O)	
	PHREEQC	TOUGHREACT
H ₂ O	0.978	0.980
Al ³⁺	−14.74	−14.63
AlO ₂ [−]	−7.19	−7.10
Al(OH) ₂ ⁺	−9.67	−9.31
AlOH ₂ ⁺	−11.78	−11.83
Ca ²⁺	−2.40	−2.59
CaCl ⁺	−3.20	−3.34
CaHCO ₃ ⁺	−3.85	−4.01
CaCl ₂	−3.68	−3.76
CaCO ₃	−5.19	−5.36
Cl [−]	−0.43	−0.40
CO ₂ (aq)	−2.51	−2.49
CO ₃ ^{2−}	−6.89	−6.90
H ⁺	−6.04	−6.04
HCO ₃ [−]	−2.85	−2.85
K ⁺	−2.65	−2.60
Mg ²⁺	−2.67	−2.96
MgCl ⁺	−2.94	−3.18
MgCO ₃	−6.07	−6.33
MgHCO ₃ ⁺	−4.11	−4.37
Na ⁺	−0.44	−0.45
NaCl	−1.36	−1.32
NaCO ₃ [−]	−7.90	−7.90
NaHCO ₃	−3.71	−3.72
NaHSiO ₃	−5.11	−5.09
SiO ₂	−2.84	−2.84
OH [−]	−6.21	−6.23

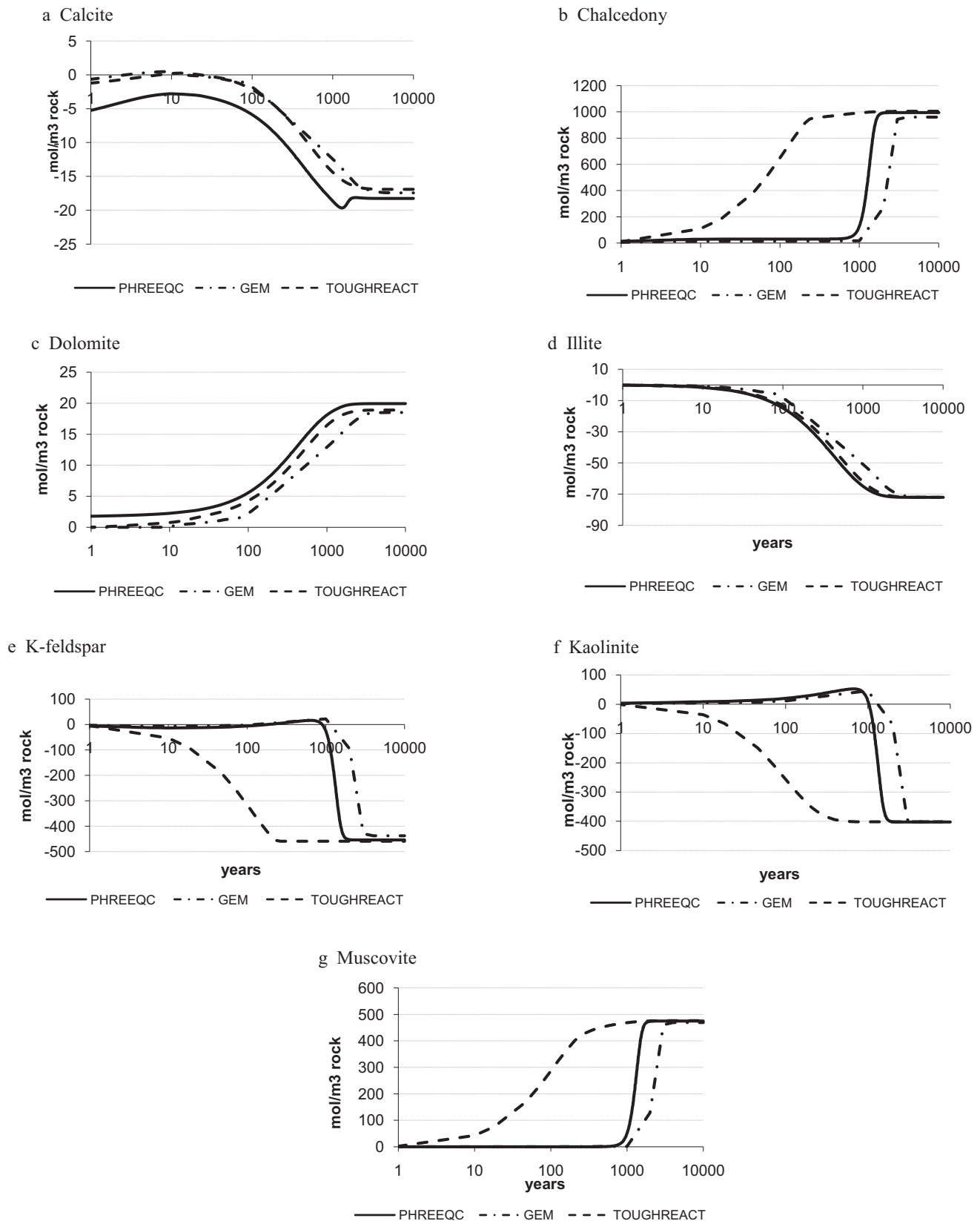


Fig. 4 – Mineral changes in moles per m³ of medium with time (positive values precipitation, negative values dissolution) for Oseberg rock type (same log *K* values are used in all three codes.).

ulation results are given in Fig. 4. With the same equilibrium constants all three simulators predicted similar mineral precipitation and dissolution in the long run, but the way in which they reached equilibrium is quite different.

The differences will most likely be due to the differences in the calculated activity coefficient and the activities. The direct comparison of the activity coefficients and activities of the aqueous species for the initial brine of the Oseberg formation, given in Table 3, calculated by PHREEQC and TOUGHREACT are given in Table 9. GEM does not output these values, hence they are not included.

No field observation or laboratory data was available to confirm the simulation results but these reactions were inferred from the diagenesis occurring in North Sea reservoirs (Bjorkum and Gjelsvik, 1988; Bjorlykke et al., 1992, 1995).

Between the three rock types studied, only one has some mineral trapping potential because of the chlorite content. Porosity did not evolve significantly throughout the simulations in any of the rock types with changes of -0.12% in Rannoch, 1.12% in Oseberg and 0.6% in Forties formation type. Although muscovite and chalcedony precipitation can have dramatic effects on permeability, and hence on the injectivity, because of the slow kinetics of these minerals, it can have only a positive effect on the enhancement of the confinement properties of the rock.

4. Conclusions

The objective of this study was to compare three numerical codes, PHREEQC, GEM and TOUGHREACT, from the point of view of geochemical modelling of CO₂ storage. The codes were applied to three target sandstone reservoirs in the North Sea. The equilibrium constants of the selected minerals, activity models, the solubility of CO₂, pH and evolution of the aqueous species and minerals in time were compared.

While large discrepancies in the calculated amount of dissolved CO₂ are found (Table 5), the pH values are in reasonably good agreement. The codes gave different results for the aqueous concentrations and the evolution of the mineral species. The discrepancies are mainly due to the differences in the thermodynamic databases and activity models. The simulations with the same equilibrium constants used in the three codes are in good agreement in the long run, but are still quite different before reaching equilibrium. Significant differences were found in the equilibrium constants used in their internal databases. This study shows how critical the selection of these data is. Hence the experience of the modeller is critical for the outcome of the modelling process. However, as was pointed out by Zhu and Anderson (2002) "...judging the quality of thermodynamic data is a job for specialists, and even they often do not agree among themselves."

Reservoir engineers have a good understanding of multiphase flow in the reservoirs, but they usually do not have extensive knowledge of geochemical modelling because geochemical processes are not as important in petroleum reservoir simulations as in geological storage of CO₂ because of the considerable time perspective for storage. On the other hand, geochemists have good experience of these processes. Therefore, collaboration between reservoir engineers and geochemists is essential for accurate prediction of fluid rock interactions during CO₂ storage.

As the kinetic data are not well known and the thermodynamic data are uncertain, the results of the geochemical

modelling should be treated as qualitative rather than quantitative. In order to verify the results, they need to be tested against experimental data and field observations. This is challenging because of the long timescales of the geochemical processes. However, the data from the early stages of CO₂ storage from field observations and experiments on heterogeneous rock samples are still valuable not only to evaluate the changes in injectivity but also to give insights in the trend of the geochemical processes. On the other hand, because of the high number of the parameters and the complexity of the processes involved in heterogeneous rocks and real brines, it is difficult to interpret the thermodynamic and kinetic data from these kinds of observations and specific experiments are needed to obtain the thermodynamic and kinetic data.

It could be easily argued that without transport processes batch modelling has limited application to the geochemical modelling of CO₂ storage, as injection of large quantities of CO₂ involves complex coupled physical and chemical processes. Although reactive transport modelling is more appropriate for proper modelling of these processes, batch modelling gives important insights into reaction paths and chemical processes in the aqueous phase, and the authors consider that it is a good starting point to build a reactive transport model.

Acknowledgements

USGS, LBNL and CMG are thanked for providing the PHREEQC, TOUGHREACT and GEM simulators respectively. The authors thank David Parkhurst and two anonymous reviewers for their comments and suggestions for the improvement of the manuscript.

References

- Audigane, P., Oldenburg, C.M., van der Meer, B., Geel, K., Lions, J., Gaus, I., Robelin, C., Durst, P., Xu, T., 2007. Geochemical modelling of the CO₂ injection into a methane gas reservoir at the K12-B field, North Sea. Special publication of AAPG on geological storage of CO₂.
- Bazin, B., Brosse, É., Sommer, F., 1997. Chemistry of oil-field brines in relation to diagenesis of reservoirs. 1. Use of mineral stability fields to reconstruct in situ water composition. Example of the Mahakam basin. *Marine and Petroleum Geology* 14 (5), 481–495.
- Bjorkum, P.A., Gjelsvik, N., 1988. An isochemical model for formation of authigenic kaolinite, K-feldspar and illite in sediments. *Journal of Sedimentary Research* 58 (3), 506–511.
- Bjorlykke, K., Aagaard, P., Egeberg, P.K., Simmons, S.P., 1995. Geochemical constraints from formation water analyses from the North Sea and the Gulf Coast Basins on quartz, feldspar and illite precipitation in reservoir rocks. Geological Society, London, Special Publications 86 (1), 33–50.
- Bjorlykke, K., Nedkvitne, T., Ramm, M., Saigal, G.C., 1992. Diagenetic processes in the Brent Group (Middle Jurassic) reservoirs of the North Sea: an overview. Geological Society, London, Special Publications 61 (1), 263–287.
- Cantucci, B., Montegrossi, G., Vaselli, O., Tassi, F., Quattrocchi, F., Perkins, E.H., 2009. Geochemical modeling of CO₂ storage in deep reservoirs: the Weyburn Project (Canada) case study. *Chemical Geology* 265 (1–2), 181–197.
- Duan, Z., Sun, R., 2003. An improved model calculating CO₂ 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.
- EC, 2009. Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009. Official Journal of the European Union, 5 June 2009.

- Gaus, I., Azaroual, M., Czernichowski Lauriol, I., 2005. Reactive transport modelling of the impact of CO₂ injection on the clayey caprock at Sleipner (North Sea). *Chemical Geology* 217, 319–337.
- Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science* 267, 729–804.
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes by high pressures and temperatures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600 degrees C and 5 kb. *American Journal of Science* 281 (10), 1249–1516.
- IPCC, 2005. IPCC Special Report on Carbon dioxide Capture and Storage. Cambridge University Press, Cambridge, United Kingdom, New York, NY, USA.
- Johnson, J.W., Nitao, J.J., Knauss, K.G., 2004. Reactive transport modelling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning. Geological Society, London, Special Publications 233 (1), 107–128.
- Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2005. Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: relevance to the integrity of a geologic carbon repository. *Chemical Geology* 217 (3–4), 277.
- Kharaka, Y.K., Cole, D.R., Thordsen, J.J., Kakouros, E., Nance, H.S., 2006. Gas–water–rock interactions in sedimentary basins: CO₂ sequestration in the Frio Formation, Texas, USA. *Journal of Geochemical Exploration* 89 (1–3), 183–186.
- Nghiem, L., Sammon, P., Grabenstetter, J., Ohkuma, H., 2004. Modeling CO₂ storage in aquifers with a fully-coupled geochemical EOS compositional simulator. In: SPE/DOE Symposium on Improved Oil Recovery, 7–21 April 2004, Tulsa, Oklahoma, SPE 89474.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One-dimensional Transport and Inverse Geochemical Calculations.
- Pruess, K., Spycher, N., 2007. ECO₂N—a fluid property module for the TOUGH2 code for studies of CO₂ storage in saline aquifers. *Energy Conversion and Management* 48 (6), 1761–1767.
- Steeffel, C.I., Lasaga, A.C., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of Science* 294 (5), 529–592.
- Svensson, U., Dreybrodt, W., 1992. Dissolution kinetics of natural calcite minerals in CO₂-water systems approaching calcite equilibrium. *Chemical Geology* 100 (1–2), 129–145.
- Thibeau, S., Nghiem, L., Ohkuma, H., 2007. A modeling study of the role of selected minerals in enhancing CO₂ mineralization during CO₂ aquifer storage. In: SPE Annual Technical Conference and Exhibition, SPE, Anaheim, CA, USA.
- Wigand, M., Carey, J.W., Schütt, H., Spangenberg, E., Erzinger, J., 2008. Geochemical effects of CO₂ sequestration in sandstones under simulated in situ conditions of deep saline aquifers. *Applied Geochemistry* 23 (9), 2735.
- Wolery, T.J., 1992. EQ3NR, A Computer Program for Geochemical Aqueous Speciation-solubility Calculations: Theoretical Manual, User's Guide and Related Documentation (Version 7.0). Lawrence Livermore Nat. Lab., Livermore, CA, USA.
- Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone-shale system. *Chemical Geology* 217, 295–318.
- Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., 2006. TOUGHREACT—a simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO₂ geological sequestration. *Computers & Geosciences* 32 (2), 145.
- Zhu, C., Anderson, G., 2002. Environmental Applications of Geochemical Modeling. Cambridge University Press, Cambridge, New York, 284 pp.