

Reactive transport modeling using TOUGHREACT for the long term CO₂ storage at Sleipner, North Sea

Pascal Audigane (1), Irina Gaus (1), Karsten Pruess (2), Tianfu
Xu (2)

(1)

BRGM, French Geological Survey, 3 Av. Claude Guillemin, BP 6009
45060 ORLEANS Cedex 2 (FRANCE)
email :p.audigane@brgm.fr

(2)

LBNL, Lawrence Berkeley National Laboratory, Earth Sciences Division, University of
California, One cyclotron Road, Berkeley, CA 94720, (USA)

Summary

The geo-chemical impact of the CO₂ injection on the Sleipner reservoir is investigated using the reactive transport code TOUGHREACT, developed at LBNL.

The modeling is performed for both the injection phase as well as the long term storage period (several thousand years). The mineralogical composition has been derived from core data from the Utsira formation, the formation wherein the CO₂ is injected (1085 m depth, Pearce et al., 1999). It is composed predominantly of quartz with minor K-feldspar, plagioclase, calcite and mica. The water composition analyzed in the nearby Oseberg formation has been used as representative of the Utsira formation water since no more accurate data are currently available. The models are initially run in kinetic batch mode in order to determine the principal geo-chemical reactions in the reservoir due to the presence of CO₂. In a second step, fully coupled reactive transport modeling is performed in order to calculate the evolution of the CO₂ plume in space and time as well as the geo-chemical impact on the reservoir. The simulations are performed for a period of time of 10 000 years covering 25 years of CO₂ injection. Simulation results predict low chemical activity in the Utsira formation with the injected CO₂ according the chosen mineralogy and the initial formation water. The major part of carbon dioxide is trapped as supercritical gas (structural trapping) and as dissolved gas in the brine (dissolution trapping). After 10 000 years, the total amount of CO₂ sequestered as mineral phase is actually slightly negative, indicating no mineral trapping takes place, due to the dominating impact of calcite dissolution over a large area.

1. Introduction

At the Sleipner field in the North Sea, CO₂ (here a byproduct of gas exploitation) is stored in an underground saline aquifer for the very first time. Seen as a way to dispose of CO₂ and avoid climate effects, this method has profound potential importance (SACS2, 2002). A group of energy companies together with scientific institutes and environmental authorities of various European countries formed the Saline Aquifer CO₂ Storage (SACS) Project consortium which aims to develop a consensus about the monitoring results and the validity of the available models and tools through an interdisciplinary approach.

Numerical modeling of geological storage of CO₂ requires the capability of simulating hydrodynamics of brines and gas coupled with chemical reactions with respect to the supercritical CO₂ injected into an aquifer with a specific brine composition and mineralogy. The numerical code TOUGHREACT (Xu *et al.*, 2001; Xu *et al.*, 2004) aims at performing such processes. Its recent development allows a complete 3D simulation model of the carbon dioxide within saline aquifer. The treatment of density changes induced by the dissolution of CO₂ in the brines is also considered providing the slow downward migration process increasing the dissolution of the gas.

2. The Sleipner site

The Sleipner area is located in the Norwegian part of the North Sea (Norwegian block 15/9) (Figure 1). CO₂ is injected into the Mio-Pliocene Utsira Sand, a highly elongated sand reservoir with an area of some 26100 km² of which the depth ranges between 700 and 1000 m. Seismics revealed the presence of several thin shale layers within the Utsira sand. Most layers have an average thickness of 1 to 1.5 m, but a single 6.5 m thick shale layer exists close to the top of the Utsira sand (Zweigel *et al.*, 2004).

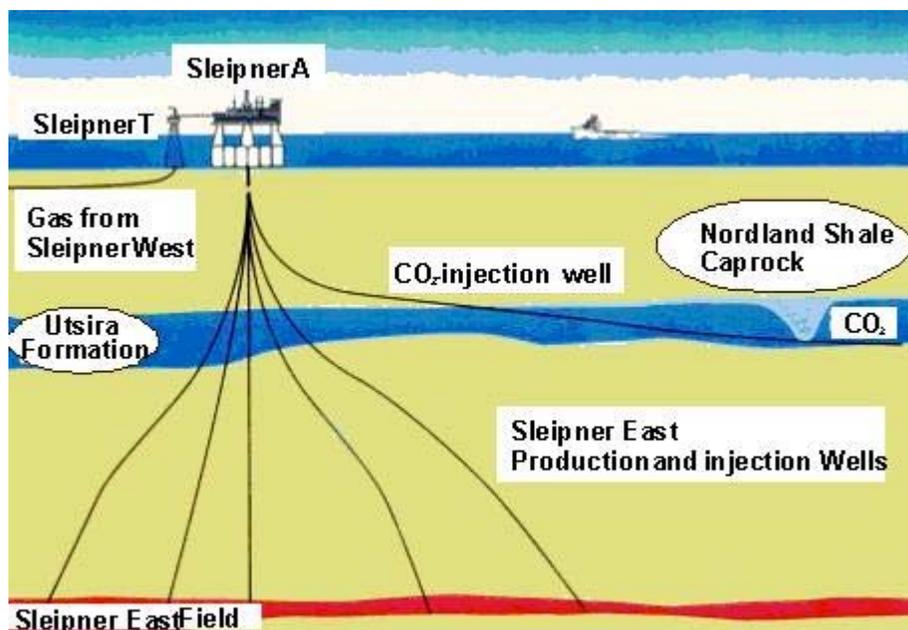


Figure 1: Cross section of the Sleipner area with CO₂-injection (SACS2, 2002).

The Utsira Sand is overlain by the sediments of the Nordland Group, which are reported to be mainly shales in their lower part and have a thickness of approximately 250 m. These sediments provide a seal for the Utsira Sands and inhibit vertical CO₂ migration, with capillary leakage of CO₂ unlikely to occur (Kemp *et al.*, 2001). Repeat seismic surveys (the most recent one took place in 2002) have shown that the injected supercritical CO₂ moves, due to buoyancy effects, upward from the injection point and accumulates under the overlying cap rock and shale layers. A near “steady state” flow upwards to the top of the reservoir seems to have been reached by 2001 and most of the CO₂ injected from 2001 to 2002 has spread laterally at the mid level and the top level (Arts *et al.*, 2004).

3. Geochemical data

Geochemical composition of the Utsira Sand

The Utsira Formation sandstone comprises a poorly cemented, fine to medium grained, moderately sorted highly porous sand (42 % porosity). It is composed predominantly of subangular to subrounded, occasionally angular, quartz grains with minor K-feldspar, plagioclase, calcite and coarse- to gravel-sized shell fragments including siliceous sponge spicules, foraminifera and radiolarian tests. Rare biotic flakes and rare glauconitic grains are present, also clay grade materials are rare. The mineralogical composition of the Utsira Formation between 1085 and 1086 m has been used (reported in Pearce *et al.*, 1999) (Table 1). Its composition consists mainly of quartz, K-feldspar, plagioclase, mica and calcite. Minor constituents are chlorite, zeolite, Ti-oxides, ilmenite and pyrite.

Mineral	Volume percentage	Modeled Mineral
Quartz	44.19	Chalcedony
K-feldspar	4.01	K-feldspar
Plagioclase	1.74	Albite
Chlorite	0.77	Clinochlore-7A
Mica	3.02	Illite
Zeolite	0.13	not modeled
Calcite	3.9	Calcite
Ti Oxides	0.02	not modeled
Apatite	0.01	not modeled
Ilmenite	0.07	not modeled
Pyrite	0.03	not modeled
Porosity	41.99	
Total	99.88	

Table 1 - Composition of the Utsira reservoir as observed in Pearce et al. (1999) and its conceptualization within the geochemical model.

For the conceptualization of the mineralogy in the geochemical model the following selections are made: clinochlore is used as representative for the chlorite group, plagioclase is modeled as albite and the phase described as mica is considered as illite. Chalcedony is selected instead of quartz. The very small zeolite fraction is not modeled, because its exact composition is not known and therefore its thermodynamic properties are insufficiently known. Also the trace minerals apatite, ilmenite, pyrite and Ti-oxides are not included in the model.

The following minerals were included as secondary minerals (minerals allowed to precipitate as a consequence of mineral interaction): magnesite, dawsonite, gypsum, disordered dolomite and kaolinite. Of course, all primary minerals are allowed to precipitate as a consequence of interaction with CO₂ in case they become supersaturated.

Formation water

No samples from the Utsira reservoir at Sleipner are available, however several samples at other locations, such as at Oseberg have been taken. A homogeneous porewater composition throughout the Utsira formation at Sleipner can reasonably be assumed and the composition selected for the modeling is based on this and is similar to the Synthetic Utsira Porewater (SUP) which is used for the experiments with the Utsira sands (Rochelle and Moore, 2002). This composition is taken as a starting point and is subsequently equilibrated using geochemical modeling with the reservoir mineralogy (chalcedony, K-feldspar, albite, illite, calcite, clinochlore-7A, dawsonite, the latter is allowed to precipitate only). Results are shown in Table 2).

Parameter	Value	Elements	Concentration (M)
Temperature (°C)	37	Al	1.30E-08
Ionic Strength	0.589	C	2.98E-03
pH	7.21	Ca	7.11E-03
pe	9.95	Cl	5.25E-01
		K	4.26E-04
		Mg	9.58E-02
		Na	3.11E-01
		Si	2.53E-04

Table 2 - Composition of the initial formation water used for the modeling after equilibration with the minerals present in the reservoir.

Thermodynamic data

For the modeling the TOUGHREACT thermodynamic database is used. It is a revised version from John Apps of the database of the EQ3/6 geochemical modeling code (Wolery, 1992).

Kinetic rates

The kinetic rate law for the dissolution and precipitation of the minerals is simplified from Lasaga (1984):

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

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

The kinetic rate constants for the selected minerals are taken from the literature. Literature data for the value of the power (n) in the rate expression are fragmentary and sometimes inconsistent. Therefore a uniform average value for n of 0.5 is selected for all minerals. Since no direct measurements of BET-surface areas are available for the Utsira reservoir, the geometric surface area is used for the calculation of the reactive surface area assuming that mineral grains are spherical (Table 3). For all the minerals, apart from the clays, an average grain diameter of 3.3×10^{-5} m is assumed. For the clays an average grain diameter of 2×10^{-6} m is taken which is the coarsest clay size. Interaction with the minerals is generally expected to occur only at selective sites at the surface and the difference between total surface area and reactive surface area can be between 1 and 3 orders of magnitude (White and Peterson, 1990). Hence, a scaling factor of 0.001 is used for all minerals to account for the difference between geometric surface area and the reactive surface area.

	Molar volume (10^{-6} m ³ /mole)	Specific surface area (m ² /g)	Rate constant (log k_{37}) (mole/m ² s)	Source of kinetic rate data
Albite	100.25	6.95E-02	-8.44	Blum and Stillings (1995)
Chalcedony (Quartz)	22.69	6.86E-02	-11.73	Rimstidt and Barnes (1981)
Clinochlore- 7A	20.98	1.13E-01	-11.63	Nagy (1995)
Dolomite-dis	64.39	6.35E-02	-7.38	Pokrovsky and Schott (2001)
Illite	59.89	4.68E-01	-13.08	set to muscovite rate (Nagy, 1995)
Kaolinite	99.52	1.16E+00	-12.54	Nagy (1995)
K-feldspar	108.87	7.11E-02	-8.79	Blum and Stillings (1995)
Magnesite	28.02	6.04E-02	-7.38	as dolomite

Table 3 - Molar volumes, specific surface areas and kinetic rate parameters at 37°C of the primary and secondary minerals in the cap rock and the reservoir.

Because reactions with respect to some carbonates (calcite, dawsonite) are very rapid, their dissolution and precipitation is modeled to occur instantaneously and no kinetics is introduced for these minerals.

Pressure and temperature conditions

The modeling is performed at 37°C, based on a temperature measurement for the shallow subsurface of the Sleipner area (Statoil data). Since there are no indications of overpressure in the Utsira Formation in the Sleipner area the pressure is assumed to be equal to the hydrostatic pressure which is approximately 100 atm.

4. Simulation approach

TOUGHREACT

All the simulations presented in this paper have been performed using the reactive transport code TOUGHREACT (Xu *et al.*, 2001; Xu *et al.*, 2004). This code, developed at the LBNL, is a derivative product from the fluid flow simulator TOUGH2 originally built for geothermal and remediation purposes (Pruess *et al.*, 1999). TOUGHREACT contains all the facilities for simulating chemical reactions taking place between species present both in the liquid phase and in the mineral phase.

The coupling between hydrodynamics and chemical reactivity is performed using a sequential iterative approach (Yeh and Tripathi, 1989) which means that for each time step the pressure field and the fluid flow associated is calculated first and used for the transport of the species between cells composing the mesh. In a second step, batch modeling is performed for each cell and an iterative procedure can be used for reducing the error induced by this sequential approach.

Special attention has been paid to correctly calculate thermodynamic values for the density, the viscosity, the fugacity and the enthalpy of the CO₂ under supercritical conditions (Pruess and Garcia, 2002). The fugacity model takes into account the salinity of the liquid phase affecting the gas dissolution. The enthalpy model controls the heat exchange with the gas phase. No temperature changes are considered in this work. A general form of rate law presented in Eq. (1) is used for the kinetics controlling mineral dissolution and precipitation (Lasaga, 1984).

The host rock minerals clinocllore, K-feldspar and illite do not dissolve significantly, the same counts for the secondary minerals kaolinite, dolomite, magnesite (volume fraction changes $<6 \cdot 10^{-4}$). Although other mineralogical compositions instead of clinocllore and illite could have been selected for chlorite and mica respectively (eg Fe-rich variations), their impact is assumed to be minor in this case because of their extremely slow reaction rates.

The global reactivity in the Utsira formation is very low based on the selected mineralogy and formation water. Albite dissolution is very slow and the chalcedony and dawsonite precipitation is very small. Because only minor mineral dissolution and precipitation occurs, the total volume of minerals undergoes little changes and the porosity is not affected.

The amount of CO₂ sequestered in the mineral phase in kg per m³ is negative until 4200 years. During this period carbonate dissolution has the largest impact. After that net mineral trapping occurs through the alteration of albite. Nevertheless, the amount of CO₂ sequestered in the mineral phase at the end of the simulation represents about $8 \cdot 10^8$ kg of CO₂ which is very small in comparison with the amount of CO₂ originally injected ($2.36 \cdot 10^{11}$ kg).

2D reactive transport model

The simplified 2D model of CO₂ injection and storage at Sleipner taking into account the shale layers provides information on the evolution of the gas bubble in space and time during and after the injection. A cylindrical geometry centered around the injection well with a maximum extension of 100 km is chosen for this model. In the vertical direction, the mesh is composed by 22 layers with four low permeable clay layers spaced by 30 meters from the top of the formation (Figure 2). The mineralogical composition of the shale layers is in this case assumed to be similar to the Utsira sand composition. The top and the bottom of the formation are assumed impermeable. The injection point is located at 940 m. All the parameters necessary for the hydrodynamics modeling are listed in the Table 5.

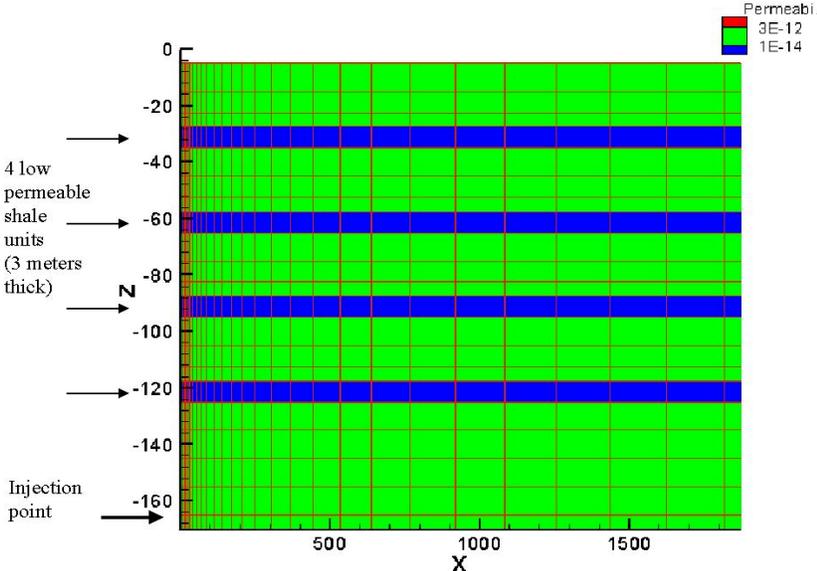


Figure 2- Representation of the mesh used for the 2D model of CO₂ injection at Sleipner. The cylindrical geometry is centered around the injection well. The injection point is located at 940 m.

Aquifer thickness	184 m
Permeability	$3.0 \times 10^{-12} \text{ m}^2$
Porosity	0.42
Temperature	37°C
Pressure	110 bars
Injection rate	30 kg s^{-1}
Relative permeability model:	
. <u>Liquid</u> (Van Genuchten, 1980)	
$k_{rl} = \sqrt{S^*} \left\{ 1 - \left(1 - [S^*]^{1/m} \right)^m \right\}^2$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$
Residual liquid saturation	$S_{lr} = 0.20$
Exponent	$m = 0.40$
. <u>Gas</u> (Van Genuchten, 1980)	
$k_{rg} = \sqrt{S_g^*} \left\{ 1 - \left(1 - [S_g^*]^{1/m} \right)^m \right\}^2$	$S_g^* = (S_g - S_{gr}) / (1 - S_{gr})$
Residual gas saturation	$S_{gr} = 0.05$
Exponent	$m = 0.40$
Capillary pressure (Van Genuchten, 1980)	
$P_{cap} = -P_0 \left([S^*]^{-1/m} - 1 \right)^{1-m}$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$
Residual liquid saturation	$S_{lr} = 0.20$
Exponent	$m = 0.40$
Coefficient	$P_0 = 3.58 \text{ kPa}$

Table 4- Hydrogeological parameters for the 2D modeling of CO₂ injection at Sleipner with TOUGHREACT.

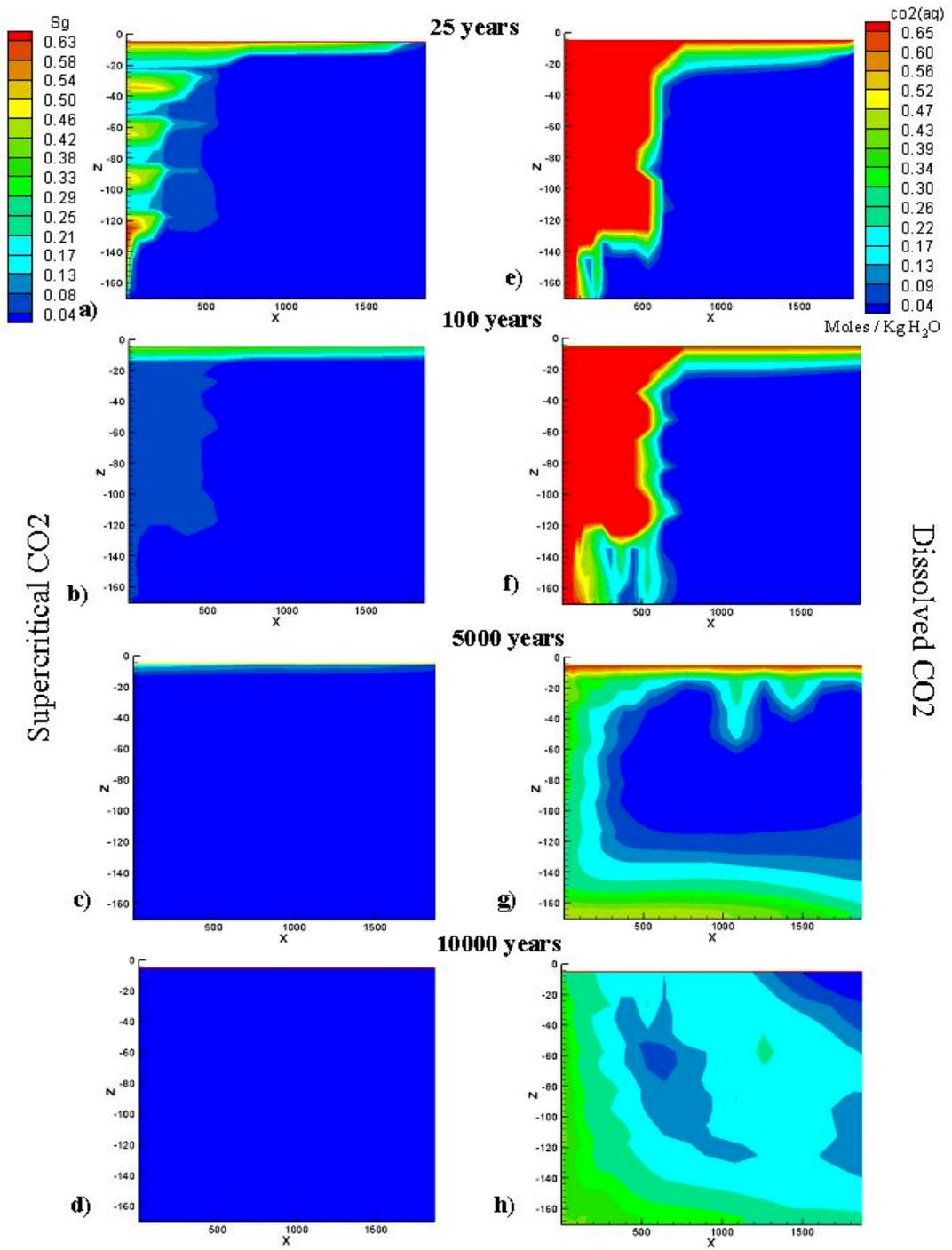


Figure 3- Supercritical CO₂ gas bubble (left) and dissolved CO₂ evolution model (right) during and after injection.

Hydrodynamics results:

After 25 years of injection, the supercritical CO₂, which is lighter than the brine, reaches the top of the formation and the gas bubble extends laterally up to 500 m away from the well except at the top where the CO₂ accumulates and extends up to 1500 m (Figure 3, a). The semi permeable layers induce some accumulation of CO₂ beneath them without stopping the upward migration. Hence after 100 years, almost all the supercritical CO₂ has reached the top of the formation while dissolving in the brine (Figure 3, b). The dissolution of CO₂ is calculated from the Henry's law assuming equilibrium between gas and liquid phase. The concentration of aqueous CO₂ is controlled by the partial pressure of supercritical CO₂: $\Phi P_{CO_2} = K_h X_{CO_2}$, with Φ the fugacity coefficient, P_{CO_2} the CO₂ partial pressure, K_h the Henry's constant and X_{CO_2} the mole fraction of dissolved CO₂ in the liquid phase. The rate of dissolution is a function of the pressure and the salinity of the media.

The density of the liquid phase during progressive CO₂ dissolution becomes higher than that of the initial brine and CO₂-loaded brine migrates downward. This density contrast is smaller than that between the supercritical CO₂ and the initial brine explaining why one can observe that the downward migration of aqueous CO₂ occurs much slower than the upward migration of supercritical CO₂ (Figure 3, e, f, g and h). This mixing of aqueous CO₂ in the liquid phase tends to accelerate the dissolution process and after 5000 years almost all the supercritical CO₂ has been dissolved (Figure 3, c), while it is completely dissolved after 10 000 years (Figure 3, d)

Chemical reaction results:

As for the kinetic batch modeling, the global reactivity at Sleipner modeled in 2D is also low. After 25 years, the pH decreases from 7.2 to 4.9 inside the supercritical CO₂ gas bubble (Figure 4, a). There is a slight dissolution of calcite (Figure 4, b) and albite (Figure 4, d) accompanied by a slight precipitation of dawsonite (Figure 4, c) and chalcedony (not shown). Minor modifications have been noticed for the other minerals.

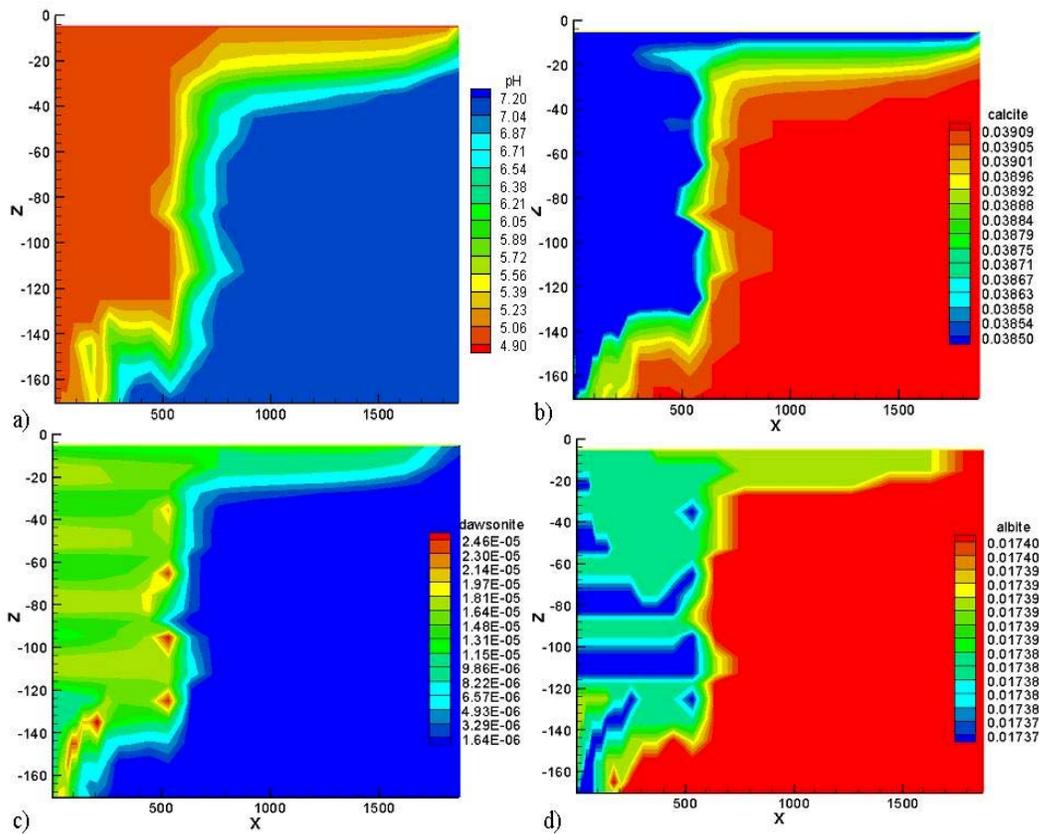


Figure 4: Numerical modeling of the pH evolution, calcite and albite dissolution and dawsonite precipitation in volume fraction after 25 years of CO₂ injection at Sleipner.

At the end of the simulations (10 000 years), the density segregation of the liquid phase due to CO₂ dissolution results in an overall downward migration of the aqueous CO₂ (Figure 5, a), accompanied by a pH decrease (Figure 5, b). The dissolution of calcite is at the maximum about 8% in volume fraction change after 10 000 years (Figure 5, c). At the same time, albite dissolution and chalcedony and dawsonite precipitation occur at a very low level (Figure 6, a, b, c). One can notice that because calcite dissolution occurs instantaneously, it occurs most intensively there where the supercritical CO₂ was initially present. For the other minerals, precipitation and dissolution are slower and in these areas where the aqueous CO₂ has moved downward because of the density increase of the brine enriched in CO₂. After 10 000 years, the total amount of CO₂ sequestered as mineral phase is actually slightly negative, indicating no mineral trapping takes place, due to the dominating impact of calcite dissolution over a large area (values of around -2 kg/m³ of medium - Figure 7).

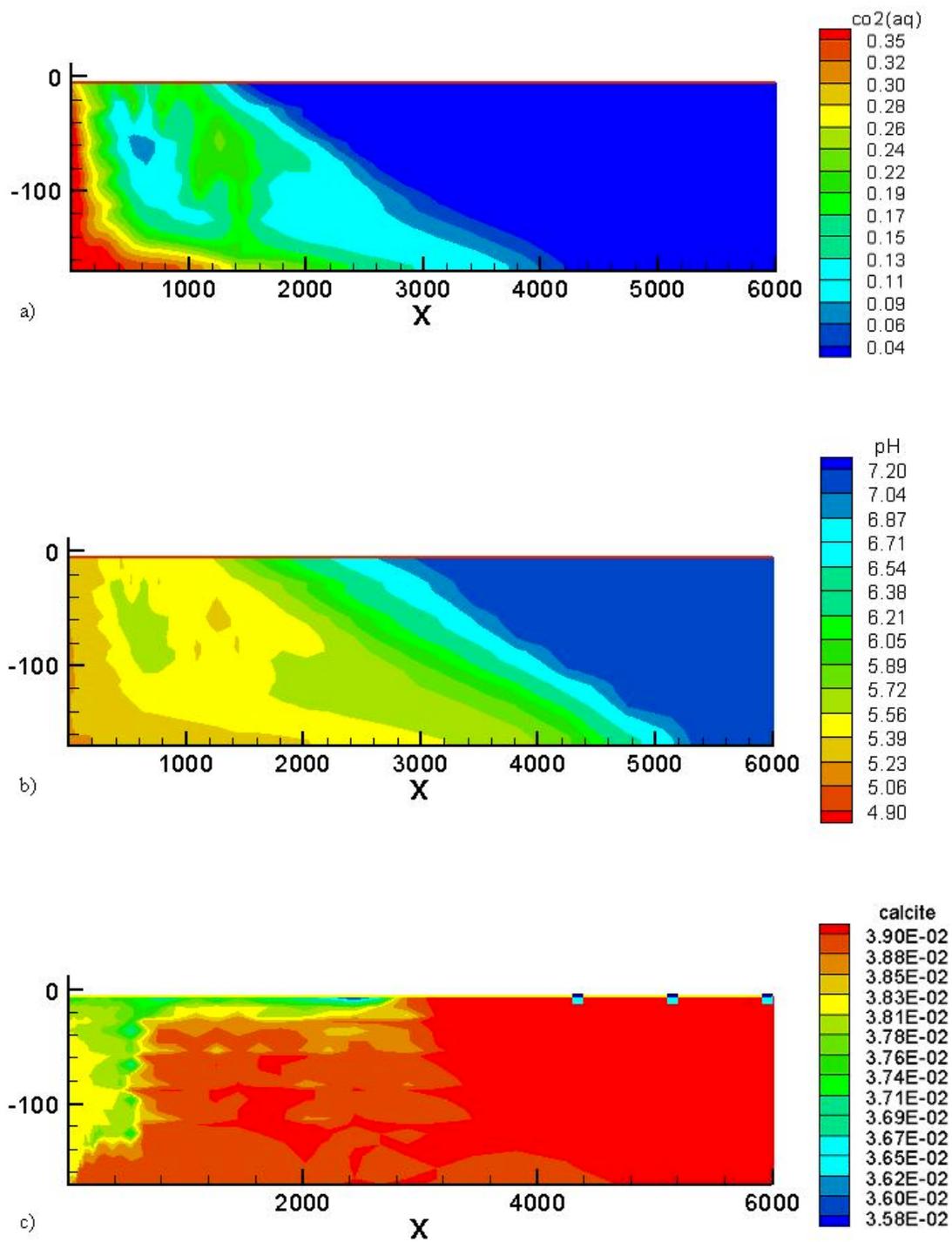


Figure 5: Numerical simulations of the dissolved CO₂ (in mol/kg H₂O), pH decrease and calcite dissolution (in volume fraction) at Sleipner after 9875 years of CO₂ injection.

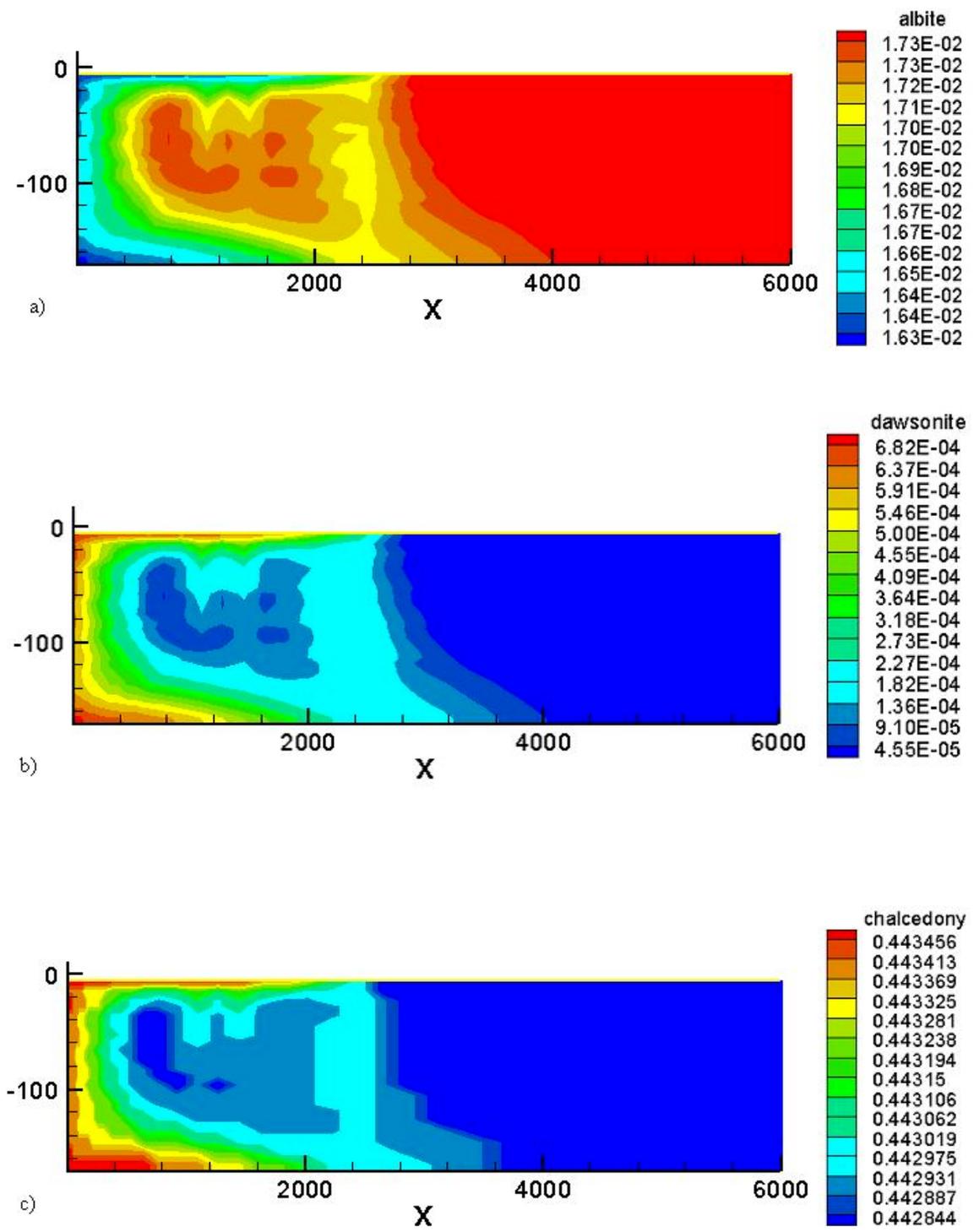


Figure 6: Numerical simulations of the albite dissolution and dawsonite and chalcedony precipitation in volume fraction at Sleipner after 9875 years of CO₂ injection.

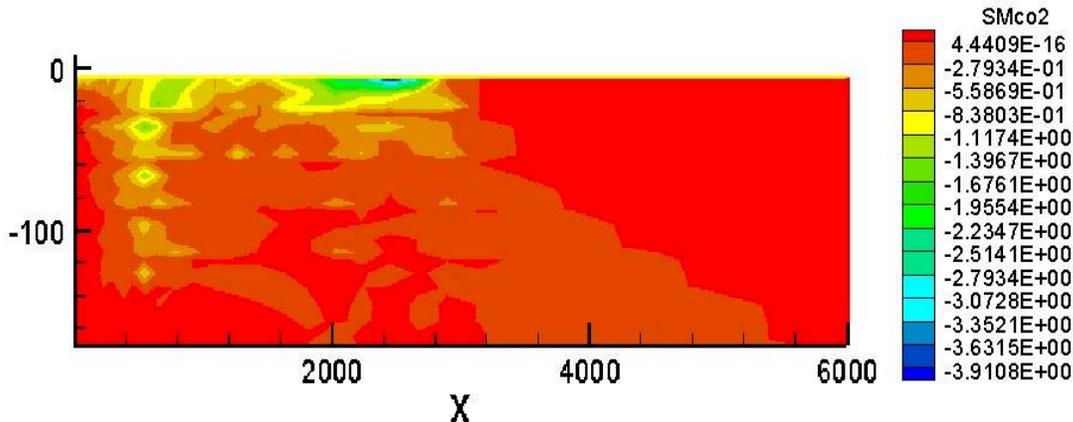


Figure 7: Numerical modeling of the CO₂ mineral sequestration at Sleipner after 10 000 years. The negative value means that dissolved carbon in the brine increases because of calcite dissolution during the storage period.

5. Future works

We have presented in this paper preliminary results for fully coupled numerical modeling of CO₂ storage processes at the Sleipner site taking into account a simplified level of reservoir heterogeneity (clay layers). Thanks to the numerical simulator TOUGHREACT, it is possible today to simulate injection of carbon dioxide at supercritical state in brines considering chemical reactions both in the liquid phase (brines) and with the solid phase (minerals). The simulations present very encouraging results revealing a low level of chemical reactivity at Sleipner because of its specific mineralogical composition.

Nevertheless, reactive transport modeling requires a complex technique of coupling the hydrodynamics with chemical reactivity. The knowledge of chemical parameters like kinetics rates and reactive surfaces areas remain poorly known for some minerals. Hence, a proper sensitivity analysis needs to be done in order to provide a variability range of the impact of the three main processes controlling the trapping of the injected CO₂: structural trapping, dissolution trapping and mineral trapping.

Acknowledgements

This work, supported by the EU and national governments, was funded by the GEOSEQ project (BRGM), and the SACS (CO₂-STORE) consortium (Statoil, BP, Exxon, Schlumberger, Progressive Energy, Energi E2, IEA GHG, NGU, Norsk Hydro Total and Vattenfall, BGS, GEUS, IFP, TNO, BGR and SINTEF).

6. Bibliography

Arts, R., A. Chadwick et O. Eiken (2004). Recent time-lapse seismic data show no indication of leakage at the Sleipner CO₂-injection site. GHGT 7-7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 5-9 September, 2004

Kemp, S. J., J. Bouch et H. A. Murphy (2001). Mineralogical characterisation of the Nordland Shale, UK Quadrant 16, northern North Sea. British Geological Survey Commissioned Report CR/01/136

Lasaga, A. C. (1984). "Chemical kinetics of water rock interactions." *Journal of Geophysical Research* **89**: 4009-4025.

Pearce, J. M., S. J. Kemp et P. D. Wetton (1999). Mineralogical and petrographical characterisation of 1 m core from the Utsira formation, Central North Sea. British Geological Survey Report WG/99/24C

Pruess, K. et J. Garcia (2002). "Multiphase flow dynamics during CO₂ disposal into saline aquifers." *Environmental Geology* **42**: 282-295.

Pruess, K., C. Oldenburg et G. Moridis (1999). TOUGH2 User's Guide Version 2.0. Lawrence Berkeley National Laboratory LBNL-43134

Rochelle, C. et Y. A. Moore (2002). The solubility of supercritical CO₂ into pure water and synthetic Utsira porewater. British Geological Survey Report CR/02/052

SACS2 (2002). Final Technical Report. EU-contract ENK6-CT-1999-00014

Van Genuchten, M. T. (1980). "A closed-form equation for predicting the hydraulic conductivity of unsaturated soils." *Soil Sci. Am. J.* **44**: 892-898.

White, A. F. et M. L. Peterson (1990). "Role of the reactive surface area. Characterisation in geochemical kinetic models. Chemical Modeling of Aqueous Systems II." *American Chemical Society*(Washington DC): 461-475.

Wolery, T. J. (1992). Software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 8.0). Lawrence Livermore National Laboratory UCRL-MA-110662 PTI

Xu, T., E. Sonnenthal, N. F. Spycher et K. Pruess (2004). TOUGHREACT user's guide: A simulation program for non-isothermal multiphase reactive geochemical transport in variable saturated geologic media. Lawrence Berkeley National Laboratory LBNL-55460

CONFERENCE PROCEEDINGS

Xu, T., E. Sonnenthal, N. F. Spycher, K. Pruess, G. Brimhall et J. A. Apps (2001). "Modeling multiphase fluid flow and reactive geochemical transport in variably saturated fractured rocks: 2 Applications to supergene copper enrichment and hydrothermals flows." *American Journal of Science* **301**: 34-59.

Yeh, G. T. et V. S. Tripathi (1989). "A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components." *Water Resour. Res.* **25**(1): 93-108.

Zweigel, P., R. Arts, A. Lothe et E. Lindeberg (2004). Reservoir geology of the Utsira Formation at the first industrial-scale underground CO₂ storage site (Sleipner area, North Sea). Geological Storage of Carbon Dioxide for Emissions Reduction. S. Baines, J. Gale and R. Worden. London, Geological Society, London, Special Publications: 165-180.