Flux of CO_2 through hydrate sealing of CO_2

Atle Svandal[*1], Bjørn Kvamme[1]

[1]Department of Physics and Technology, University of Bergen,
Allègaten 55, N-5007 Bergen, Norway

Introduction

Storage in reservoirs is today one of the most promising approaches for safe long terms storage of CO_2 as a means for reducing the emissions to the atmosphere. Above relevant storage reservoirs, such as the proposed CO_2 injection in the Snøhvit field, where the seafloor is sufficiently deep and the sea temperature is sufficiently low, there will be a zone of hydrate stability. In this region gas hydrates may form and provide an additional sealing effect that reduces the leakage of CO_2 from the reservoir. With a sealing hydrate layer the net flux of CO_2 into the ocean will be determined by the dissociation of hydrate towards an aqueous phase since the heterogeneous formation of the hydrate film on the CO_2/water interface is significantly faster. The reduced mass transport across the hydrate results in a non-stationary situation of hydrate formation on the CO_2 side and hydrate dissociation in gradients of CO_2 chemical potentials on the other side. Given a solid hydrate layer, the transport of CO_2 above the layer will no longer be a rising plume but a much slower process with the CO_2 dissolved in water. The hydrate sealing effect can only be temporary, but the effective extension of the storage time may be considerable. This scenario of a CO_2 hydrate dissociating into the ocean is very similar to natural gas hydrate reservoirs which are partly exposed towards the seafloor. As a greenhouse gas, methane is in the order of 25 times more aggressive than CO2. It is therefore also an important global challenge to be able to make acceptable predictions of the dissociation flux of methane from these reservoirs.

A diffusion controlled dissociation

Shown in Fig.1 is the hydrate stability curve for the CO_2 hydrate and the geothermal gradient with a seafloor at 400 m and a sea temperature of 1°C. The crossing of these curves represents the lower limit for hydrate stability, which is around 630m for this example.

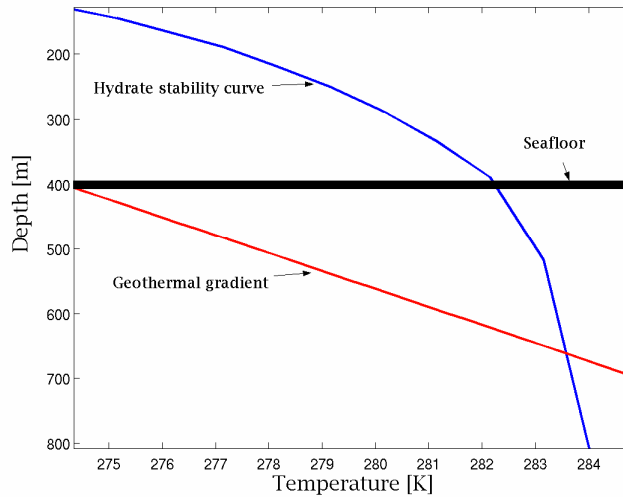[*] Corresponding Author: atle.svandal@ift.uib.no, +47 55583258

Figure 1. Hydrate stability curve of CO2, and a geothermal gradient of 0.036 C/m.

Results from our work on modeling the hydrate by a phase field theory suggests that the dissociation is governed by the diffusion in the aqueous phase. With a very simple model with a hydrate layer at 600 m, assuming liquid diffusion through the seabed and pure water at the seafloor a flux can be estimated from the Fick's law of diffusion, Eq. 1. Phase field simulations shows that the mole fraction of CO_2 at the aqueous side of the interface takes the equilibrium value between water and hydrate which at 600m and 8 °C is 2.5%.

$$J = -D\frac{\Delta c}{\Delta x} \tag{1}$$

The diffusion coefficient $D=10^{-9}$ m^2/s in the aqueous phase. This gives a flux that corresponds to about 10 g/m^2/year. With a diffusion of CO_2 through the hydrate layer this system can attain a static situation where the flux through the hydrate is equal to the flux through the 200 m of seabed. The diffusion coefficient in hydrate is in the order of 10^{-3} smaller than in the water. If such a situation is obtained a hydrate layer with a thickness about 50 cm should be expected.

We will in a similar manner make correlations between results obtained at the micro-level with phase field simulations to other macroscopic scenarios such as the formation of a hydrate layer below a clay layer and hydrate directly exposed towards the ocean. In this specific situation the transport of CO_2 away from the interface and through the clay layer is significantly lower due to the low diffusivity of fluids through the clay layer. This will reduce the rate of destruction of the clay layer through reactions between CO2 and the clay minerals, as well as through replacement of water with CO_2 and corresponding potential embrittlement/fracturing.

Conclusions

We have shown how thermodynamic properties and results obtained from phase field simulations can be used to determine flux rates from a hydrate sealing layer as well as predicting how well we can expect the hydrate sealing effect to be.

Abstract GHGT-8

2

References

Svandal A., Kvamme B., Grànàsy L., Pusztai T.: The Influence of Diffusion on Hydrate Growth. J. Phase. Equilib. Diff., in press, **26**(5), 2005.

Svandal A., Kvamme B., Grànàsy L., Pusztai T.: The phase field theory applied to CO_2 and CH_4 hydrate. J. Cryst. Growth. in press, 2005.

Kvamme B., Graue A., Aspenes E., Kuznetsova T., Grànàsy L., Tòth G., Pusztai T. Tegze G.: Kinetics of solid hydrate formation by carbon dioxide; Phase field theory of hydrate nucleation and magnetic resonance imaging. Phys. Chem. Chem. Phys., **6**, 2327, 2004.