Interactive comment on "A coupling alternative to reactive transport simulations for long-term prediction of chemical reactions in heterogeneous CO2 storage systems"

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General comments

The paper "A coupling alternative to reactive transport simulations for long-term prediction of chemical reactions in heterogeneous CO_2 storage systems" evaluates the one-way coupling method suggested in Klein et al. (2013) and progress by highlighting the general limits of this model. The paper is well written and contains several aspects that are of great interest for CO_2 storage and reactive transport modeling in general. First, the paper highlights the challenges in doing fully-coupled reactive transport simulations on complex geometries and at large scales and shows the benefits of running separate finely discretized 3D fluid-dynamic simulations and 0D reaction path calculations, and later couple the transport and reactions analytically. Second, the paper compares results from the de-coupled method with a fully-coupled (TOUGHREACT) for simple and more complex geometries, and thereby illustrates well the quality of the coupling scheme. One interesting conclusion is that, despite the limited reactivity at the low temperature (15,000 years to dissolve the chlorite to completion), reactions affect the spread of the plume. It is therefore of great interest to build on this work and use the same method on geometries that will allow more CO_2 migration (i.e. sloping aquifers), and reservoirs at higher temperatures and with more reactive mineral assemblages. The scale of the injection should also be investigated further, with the aim to use the method for large-scale simulations (tens of Mt/a scenarios). The paper is a very good basis for further studies and shows the importance to include mineral reactions to assess the safety of a CO_2 storage site. One aspect that could have been discussed in more detail is the orders-of-magnitude uncertainties in reaction rates (see Hellevang and Aagaard, 2013) (although the authors do mention it and include a sensitivity study on the reaction rate constants).

Specific comments

A threshold value for the onset of CO_2-induced reactions was defined in the model, and the modeling is seen to be quite sensitive to the choice of the threshold value. I will claim that the use of such an threshold value is artificial and that it can be avoided by proper defining the kinetics of the reaction and the initial formation water chemistry. CO_2-induced reactions are mainly caused by a drop in pH, leading to destabilization of the primary minerals in the system. The pH drop also leads to increased far-from-equilibrium reaction rates. Prior to CO2 injection most (all?) reservoir mineralogies will change at a steady-state rather than being at equilibrium, but the reactions are very slow. Any perturbation of the system, being it by CO2 injection or temperature changes, will cause some increase in rates and the system will

approach new steady-states. I would therefore suggest, as a continuation of this work, to examine the possibility of establishing such a low-reactivity steady-state before doing the CO_2 perturbation. One way may be to equilibrate the mineral assemblage with the formation water, but caution has to be made as some phases will not be at equilibrium.

One topic that could have been discussed further is simplification of the rate equations in fully-coupled simulations. It has been suggested that if the reactions consuming CO_2 are identified (in this case the dissolution of chlorite and supply of Fe^{2+}), and the dissolution reactions will be at some distance from equilibrium during the entire run, the dissolution of the source mineral and the corresponding consumption of CO_2 may be solved analytically with a first-order-decay equation (see Hellevang et al. 2013). This may allow fully coupled large-scale simulations and could in some cases be a better alternative than the one-way coupling.

It is statet that the time scale of mineral alteration is always much larger than that of hydrodynamic processes. This is not always true. One process that was not discussed in the paper is salt precipitation induced by the injection of dry CO2. This is very fast and is suggested to be the reason for the strongly reduced injectivity as observed for the Tubåen Fm. (Snøhvit) with a similar salinity to Ketzin (Hansen et al., 2013).

Page 9. Is the use of Sw in equation (3) problematic at low Sw values?

Page 13: How well can the ECO2 TOUGHREACT module estimate aqueous CO2 solubilities in high-salinity brines?

Technical corrections

Page 3, final paragraph: Strange to start the paragraph with 'However'? Implies that this is a continuation of the previous paragraph?

Page 8. In the description of equation (1) the α and β parameters are referred to as fitting parameters. This is not entirely true. These parameters may be regarded as empirical, but Lasaga and co-workers have suggested physical mechanisms for these, such as deviations from the true TST when the density of defects starts influencing the rates.

Page 14: I would suggest to remove dolomite from the secondary mineral assemblage as it is not likely to form at these conditions. Alternatively, you could discuss this and propose that some solid-solution (FeMgCa-carbonate) is more likely to form instead, but that the total carbonate formed will be quite the same if you use siderite + dolomite, or some solid-solution phase such as ankerite.

Page 20 (and some other places). The word 'cloud' is used for the free CO_2 instead of the more common 'plume'.

References

Hellevang et al., 2013. IJGGC 15, 3-15

Hellevang & Aagaard, 2013. Appl. Geochem. 39, 108-118.

Hansen et al., 2013. En. Proc. 37, 3565-3573.