

Interactive comment on “A coupling alternative to reactive transport simulations for long-term prediction of chemical reactions in heterogeneous CO₂ storage systems” by M. De Lucia et al.

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Received and published: 28 November 2014

We are grateful for the punctual suggestions and the comments by H. Hellevang, which greatly help us improving the manuscript.

1. Comment: *It is therefore of great interest to build on this work and use the same method on geometries that will allow more CO₂ migration (i.e. sloping aquifers), and reservoirs at higher temperatures and with more reactive mineral assemblages.*

We agree. Even the presented case study could be further enhanced by grid refinement. However, at the moment the computational costs for achieving fully coupled simulations on much more complex 3D models are not affordable; this would be crucial

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for assessing the discrepancy obtained with the simplified coupling, which is the purpose of this work. As for testing the method on other settings, we fully agree. We will better clarify these points in the introduction.

The investigated system is the Ketzin anticline, and the upwards migration of CO₂ after injection stop due to buoyancy and sloping is significant. This is described in section 4.1 (p 6232, line 11). The system is therefore a good benchmark for the coupled simulations under this point of view. This point needs to be better clarified in section 3.2.

2. C: *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).*

In our opinion the scale of injection will not significantly affect the applicability of the simplified coupling, however we can only speculate on this subject at this point. If anything, larger reservoirs with much larger injected mass of CO₂ than in the Ketzin-analogue system studied here would probably lead to a predominant and longer lasting presence of CO₂ in a separate phase, which would be a favorable case for the "a posteriori" evaluation of chemistry as demonstrated in the paper. This consideration will be included in the discussion.

3. C: *The paper is a very good basis for further studies and shows the importance to include mineral reactions to assess the safety of a CO₂ 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).*

We definitely agree with this comment. Long-term safety of underground CO₂ storage can be ensured only by proper assessment of the induced chemical processes, however uncertain our current knowledge may be concerning (among others) reaction rates. Such uncertainty constitutes actually one of the most important motivations for our work: for us it is crucial to be able to rapidly assess sensitivities, which is at the

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moment unfeasible with fully-coupled simulations running for months. These reasons need to be better stated and highlighted in the introduction of the paper (pag 6219).

4. C: *A threshold value for the onset of CO₂-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.*

We only partially agree with this comment. The primary function of the threshold is to filter out the overestimation of the reservoir volumes exposed exclusively to tiny amount of dissolved CO₂ given by the pure hydrodynamic simulations. The necessity of the threshold arises not from the particular chemistry and kinetics applied to the system, but from the non-reactive transport simulations. The comparison between fully coupled and non-reactive simulations (cfr figures 3, 4 and 5 and the explanation starting from pag 6233) confirm that the latter predict much larger reservoir volumes containing, at a given time point, tiny dissolved CO₂ concentrations. Those are not present in the fully coupled ones, due in part to the feedback chemistry-transport which immobilizes or consumes CO₂, but also to numerical dispersion and to the large element volumes of the employed discretizations.

We agree that the simplified coupling is sensitive to the threshold value, and that in a real life applications such threshold is unknown and must be estimated separately. This is clearly stated throughout the paper and especially in section 5.1.

5. C: *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 CO₂ 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.*

This valuable suggestion will be discussed in the discussion/future work part. In our experience, even with complete initial equilibrium or a carefully evaluated/"engineered"

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initial state, the fully coupled simulations obtain only a moderate gain in efficiency.

6. C: *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 CO₂ are identified (in this case the dissolution of chlorite and supply of Fe²⁺), 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 CO₂ 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.*

While again deeply agreeing with this comment, the purpose of the paper is to demonstrate that it is feasible to substitute, under clearly stated conditions, fully coupled reactive transport simulations with an "a posteriori" coupling of independent non-reactive simulations and geochemical batch models. We claim that this does not depend on the actual chemistry of the system, as long as it falls within the scope of the initial assumptions (more on that point in the following comment), and the construction of the case study confirms this.

We need, as suggested, to specify that simplifications of the reaction rates could lead to massive enhancement of the computational efficiency of fully coupled simulations. This was exactly the reason for us to include the Hellevang et al., 2013. IJGGC reference in section 5.2.

7. C: *It is stated 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).*

We agree that such a statement about all chemical processes would be imprecise. Our

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explanation of the hypotheses underlying the ratio of our simplified model refers to "a typical underground CO₂ storage" (pag 6220, line 11) and to the fact that the relevant mineralization (meant: alteration in the rock constituents) is typically kinetically limited. We will clarify that "relevant" means large enough to significantly change porosity and/or permeability of the host rock.

It is however true that we did not mention the salt precipitation and dry-out effects of CO₂ in our paper. This has many reasons: firstly, it is a transport-limited process at least for the salinity of the investigated brine; it would therefore violate the basis assumption of the applicability of the simplified approach (which has to be kinetically controlled). Secondly, the coarse discretization adopted for the case study would not be appropriated to estimate such a very local process, since it can be expected only in the the immediate proximity of the injection well. Thirdly, specific assessment in case of Ketzin (Baumann et al., 2014) modeled a moderate, spatially concentrated and probably only transient precipitation of salt around the injection borehole. No direct observation of salt and no repercussion on the well injectivity has been observed in Ketzin. Fourthly, a hypothetical loss of injectivity would be a problem during the operational life of the storage but it will not significantly affect the chemistry at reservoir scale, whereas our focus is on long-term scenarios. For these reasons we willingly disregarded this phenomenon.

All these issues need of course to be stated in the introduction.

Baumann, G., Henniges, J., De Lucia, M., 2014. Monitoring of saturation changes and salt precipitation during CO₂ injection using pulsed neutron-gamma logging at the Ketzin pilot site. *International Journal of Greenhouse Gas Control* 28, pp. 134–146.

8. C: *Page 9. Is the use of S_w in equation (3) problematic at low S_w values?*

It would be, but in practice if there is no water in the porous media, the whole hydrogeochemical approach as treated in the paper by softwares like PHREEQC or TOUGHREACT would not be applicable at all: we would fall in a case where the model assump-

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tions are violated. In the praxis, completely or nearly completely dried-out elements in siliciclastic reservoirs could happen only in the vicinity of CO₂ injection wells even in case of depleted gas reservoir. Obviously, however, the less water is present the less amount of reactions are possible, so that excluding those elements from the calculations would not affect significantly the outcome at reservoir scale.

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

The ECO₂N module follows an approximation of the Spycher Pruess (2005) model for CO₂ solubility and achieves good precision, at the investigated temperature of 35 C for brines up to a ionic strength of 6 molal if Na/Cl dominated, which is the case of our study.

Spycher N., Pruess K., 2005. CO₂–H₂O mixtures in the geological sequestration of CO₂. II. Partitioning in chloride brines at 12–100C and up to 600 bar. Geochim Cosmochim Acta 69(13), pp. 3309–20.

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

Corrected.

11. C: *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.*

Agreed. We will correct accordingly.

12. C: *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*

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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.

We agree that a FeMgCa-carbonate solid-solution is what actually is more likely to form (ADD citations) but, including just some end-members, for numerical reasons, represents an acceptable approximation in the end.

It is important to stress the fact that the actual chemistry simulated here is just exemplary and its nature does not affect the validation of the simplified coupling which is the focus of the paper. The focus is on how to simulate things, not what to simulate.

Interactive comment on Geosci. Model Dev. Discuss., 7, 6217, 2014.

GMDD

7, C2502–C2508, 2014

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