

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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We would like to thank the anonymous reviewer for the valuable and precise comments. We hope we addressed exhaustively all of them and look forward to submit a revised version of our paper.

1. Comment: *The authors have demonstrated the feasibility of a cheap one-way coupling approach for modelling reactive transport as an alternative to the expensive fully-coupled one, which requires many geochemical calculations. However, the presented approach relies heavily on the assumption that the major chemical composition of the fluid and rock does not change over the years that follow CO₂ injection and its migra-*

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tion, so that the reactive effects can be later incorporated by solving a reaction path problem from which a proper scaling (depending on an exposure time to dissolved CO₂) is used to determine the actual chemical composition of the fluid and rock.

Correct. The "a posteriori" coupling is valid if the feedback between transport and chemistry is limited, either because of the different time scales of the processes, or because of the non substantial alteration of fluid and host rock due to chemical reactions at the given time scale. This is a clear hypothesis and we claim that this condition is met in many CO₂ storage scenarios. If the above condition is not met, there is no way to un-couple hydrodynamics and chemistry.

2. C: *(Figures 4 and 5) start to show substantial deviations from the fully-coupled approach for times after 300 years, which shows the one-way coupling scheme misses the opportunity to capture a more realistic distribution of dissolved CO₂ over the reservoir.*

The figures display the total reservoir volumes exposed to CO₂ in time. They show that the estimates of gaseous CO₂ are in good agreement between non-reactive and fully-coupled simulations, while only the volumes exposed only to dissolved CO₂ are significantly different. Intuitively, such discrepancy is to be imputed to the fact that the non-reactive simulations are of course conservative (no CO₂ consumed), so that the exposed volumes at one given time point will always increase. However, these concentrations tend to be tiny (this is also why the method is so sensitive to the threshold value) and, given the very large elements we had to use for the simulation grid, we believe they are for a large part unphysical. To this matter, it is very important to be able to simulate heterogeneous reservoirs with finely discretized grids, but again, this is not feasible with fully-coupled simulations. The one-way coupling gives us the opportunity to do that.

3. C: *Despite this issue, the authors show in Figure 6 and 7 some good matching of their reaction path calculation, for some given grid point, with the evolution of the*

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chemical system from the fully-coupled approach for 2000 years. What is the behaviour of your estimates for times greater than 2000 years? Do every grid point behaves the same as the one shown in Figures 6 and 7?

A measure of the discrepancy between the fully coupled and the one-way coupling is given by the "self similarity" and its analysis. At least 95 and 99 which is even much better than the case of figure 7 where the similarity is above 50.

Our fully-coupled simulations reached 2300 simulation years and run into convergence and numerical problems afterwards, so that we are not able to say what they could predict in the following years. However, at a given simulation time the hypothesis of negligible feedback between chemistry and transport would be violated, so that overall the one-way coupled approach cannot be further applied. Something similar is stated at pag. 6237 starting from line 6. We will add clarification to this issue into the method's description (section 2.1).

4. C: *Because the total reservoir volume exposed to dissolved CO₂ is considerably greater in the one-way coupling approach, why don't we see this affecting Figures 6 and 7?*

Figure 6 and 7 are exemplary elements from the homogeneous and heterogeneous simulations. These figures show that the fully-coupled simulations predict a self-replicating reaction path, with good approximation. The elements which have not been exposed in either the fully-coupled or the one-way coupling would have one of the two chemistry inactive. This has been again treated with the similarity analysis: these mismatched elements are included there, since they have a non-zero discrepancy concerning the calculated CO₂ mineralization.

5. C: *Page 6220, line 15: This statement is not true for highly reactive rocks, such as carbonates. In a carbonate reservoir, important mineral alterations should be expected to occur at the time scale of the hydrodynamic processes. The feedback between flow and geochemical reactions in this case cannot be neglected. Please specify the type*

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of reservoir this work is aimed to.

We agree. We intend these bullet points as the hypotheses which need to be met for the applicability of the one-way coupling. We will express these characteristics in a more stringent and precise way.

We would like to think that the un-coupling we investigated is not limited to a specific system, even if we had some in mind: specifically, CO₂ storage in siliciclastic reservoirs such as, in Germany and northern Europe, in Rotliegend, Bundsandstein or Keuper. However we agree that a concise and clearer statement about specific target reservoirs needs to be added in this paragraph.

6. C: *Page 6220, line 25: Again, this cannot be generalized to all types of reservoirs. The porosity and permeability of carbonate reservoirs in regions rich in dissolved CO₂, and consequently with high acidity, should experience large variations that can in fact affect the hydrodynamic processes at short time scales.*

Agreed. As for the previous comment, this point needs to be read as a hypothesis that needs to be met and not as a general statement for all possible reservoirs. We will reformulate this paragraph in order to clarify these issues.

7. C: *Page 6221, line 10: How does this one-way coupling of Klein et al. (2013) used by the authors to decouple the chemical processes from the transport equations differs from the classical operator splitting scheme so commonly used to solve coupled partial differential equations with multiple chemical and physical processes? The literature is very rich with such strategies.*

Well, the one-way coupling we investigate here could be indeed defined as a radical "operator splitting" approach, since it evaluates flow and transport separately for the whole simulation time, and applies chemistry only in the end. The fully coupled simulator we adopted (TOUGHREACT) is a classical sequential non-iterative operator splitting simulator, which evaluates chemistry after each time step of flow and transport

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calculation. This concept can be easily integrated in section 2.1 in order to clarify our approach.

The cited reference compares operator splitting with a global implicit approach, in which in practice the transport equations contain source terms which directly express the chemical reactions, so that only one system of differential equations is solved at each time step for all the hydrodynamic and chemical processes simultaneously. It can be considered more precise than operator splitting, but in practice its applicability is much more limited by its computational costs for complex chemistry, and therefore it does not find wide application in the community. For example, we are not aware of global implicit simulations addressing reservoir-scale 3D simulations of underground CO₂ storage with a comparable chemistry and in any case we would not be able to produce them at the moment. We believe that this discussion falls outside the scope of our work. We could nevertheless include a concise reference to this matter in the discussion.

8. C: *Page 6221, line 20. Here it is very important that a more detailed description of the calculation steps be provided. The expression exposure time appears here for the first time after the abstract. Please explain this in the preceding paragraph.*

We agree. We will reformulate this whole paragraph adding details and precise definitions of such concepts (we refer also to following comment 10). In particular, the "exposure time" of each element is the amount of time the element contains a non-negligible amount of the injected CO₂, either in dissolved or in gaseous form. The threshold value on the dissolved CO₂ obviously affects also such exposure time: we consider "arrival time" of CO₂ in the element as the moment in which its dissolved concentration trespasses the threshold.

9. C: *Do your hydrodynamic simulations account for dissolution of gaseous CO₂ in brine? How is this done? I believe these hydrodynamic equations should be written in the manuscript (at least as an appendix section) to describe the physics and chemistry accounted for (dissolution of gaseous CO₂ is also a reactive process).*

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Yes, the non-reactive simulations account for mutual solubility of CO₂ in saline brine and of H₂O in CO₂, following the model of Spycher et al. 2005. They also consider salt precipitation but this does not occur in our models. We fully agree that those are actually "reactive processes" and that we need to clarify this information in the revised paper.

We could also include a concise appendix with the important equations for readability and clarity, but we believe that a more adequate introduction with more precise citations and references pointing at the simulator's authors work would suffice. TOUGH2, TOUGHREACT, the module ECO2N are in fact quite common and yet another summary of the underlying equations would be in our opinion repetitive; that is also the reason why we skipped many explanations in the first place.

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

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), pp. 1761–1767.

Xu et al, 2011. TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions, *Computers Geosciences* Vol. 37, pp. 763–774.

10. C: *What is characteristic water saturation? I could not find the definition of this expression in the manuscript. Please explain a bit further how the computation of this special water saturation and concentration of dissolved CO₂ during exposed time is done.*

We agree. The "characteristic saturation" (cf page 6223 line 15) is the minimum water saturation reached in the element during the exposure time (or, in converse, the

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maximum saturation reached by the CO₂-rich phase). This notion is actually important and a lot of work has been put into this analysis, since it directly affects the scaling of chemistry in case of gas saturation (cfr equation 13) and the maximum allowable CO₂ mineralization for the elements exposed only to dissolved CO₂. Each element, in fact, during its exposure time to CO₂ is actually exposed to dynamically changing concentration of dissolved CO₂ or saturations of gaseous CO₂. Which value should we consider? We compared average, time-weighted average, median and maximum values we found out that the latter should be retained as characteristic, in the sense that it controls the outcome of the chemistry. This explanation will be added section 2.1.

11. C: *Page 6224, line 10. More explanation about this analytical scaling is necessary here for a better understanding of the introduction of the reactive processes in the simulation. Please provide more information on why this is necessary to enhance the clarity of the manuscript. What is the limitation of this approach? Can this be extended to more complex chemical systems, with heterogeneity throughout the reservoir (in both fluid and rock)?*

Starting at pag 6223, line 6 we introduce the meaning and necessity of the scaling equations. We could put this introduction and further elaborate on that directly at the beginning of section 2.2, in order to have all informations concerning this matter in one place.

The scaling equations, as stated throughout section 2.1 and 2.2 in the manuscript, descend from the particular form of kinetic law assumed for the reactions and for the chosen parametrization of quantities such as the minerals' specific reactive surfaces. Since all equations in geochemistry are expressed per unit mass of solution, if one wants to actually calculate the total reaction in a given volume of rock, a scaling is needed considering the total water present in the rock volume, the total reactive surface of each minerals available for reactions and so on. Since we are considering homogenous volume fractions of minerals in each element (cfr pag 6224, line 1), such

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scaling is only dependent on porosity and water saturation, as we show in section 2.2. We will reorder and reformulate sections 2.1 and 2.2 in order to clarify in a more logical manner all these informations.

12. C: *Change explicitly to explicitly in page 6225, line 15.*

Corrected.

13. C: *Change starts to start in line 10 of page 6232. Also improve the grammar in this line.*

We would correct it this way: "After injection, the CO₂ would rapidly start its upward migration towards the anticline top, spreading and progressively dissolving in the formation brine along its way."

14. C: *Why not use pH as the control variable for measuring reactivity instead of concentration of dissolved CO₂? The pH at every element could be obtained by using some correlation model on the concentration of dissolved CO₂ (so that you don't need to perform the expensive chemical equilibrium calculations to determine it). One could claim that the more dissolved CO₂ in the brine, the higher its acidity and so its reactivity. However, if brine contains some dissolved carbonate minerals, then you can still have a concentration of dissolved CO₂ above your prescribed threshold, but the pH of brine is perhaps not acidic enough to cause substantial reactions with the rock-forming minerals. By using pH as the control variable, it should be easier to come up with a threshold that indeed reflects the reactivity of the system.*

This is a valuable suggestion. We had indeed considered the pH as possible control variable, but we soon recognised that the pH value alone would not suffice for all needed purposes. In fact, the application of the one-way coupling would still require the characteristic values of dissolved CO₂ concentration (to limit the amount of mineralization in the element) and the characteristic gas saturation (for the scaling). Considering the pH as control variable would indeed be more understandable from a

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chemical point of view, but will introduce a third variable, highly correlated with the first two, and therefore somewhat redundant from a practical point of view. Since the correlation between pH and dissolved CO₂ holds, we could translate the original threshold into the corresponding pH values, adding this discussion, i.e., in section 2.1. A further argument is, as also the Reviewer points out, that the presence of local carbonate buffer could push the threshold over which reactions start to happen, making the use of pH really depending on the chemistry and mineralogy of the investigated system, whereas the use of CO₂ is not.

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