

Please accept my apologies for the delayed review!

Dr. Roded presents an analytical solution-based analysis of reactive, thermal (horizontal, radial and planar) flow resulting from injection into a thin aquifer confined between impermeable rock. This is a follow-up to a previous study (Roded 2024b) and declared to analyze the effect of simplifying the full kinetic treatment with an equilibrium reaction assumption in cases that can be considered transport-rather than reaction rate-controlled.

While the overall results seem to be potentially useful, I have a number of critical remarks on this contribution and I strongly recommend applying major revisions to make this paper more approachable and useful for the community:

1. Simple to correct, but utmost important: the units of the injection rate,  $Q$ , immediately appeared wrong. I quickly communicated with the author about this to simplify the review process and, indeed, instead of 500 m<sup>3</sup> per *second*, they were taken as 500 m<sup>3</sup> per *day* in the reported calculations (i.e., wrong by ca. 4 orders of magnitude). This needs to be corrected in Table 1 (easy) and I strongly recommend to also post a corrigendum to the previous paper where the same mistake occurs.
2. Not so simple and very important: Over large parts of the manuscript the difference to Roded (2024b) is not apparent and the texts are very similar and Figures identical or very similar as well. A revision should make much clearer how the simplifying equilibrium assumption is actually implemented and modifies the previous work. Namely, the derivation of the analytical solutions is essentially identical up to ca. equation 15 and then, without explanation, equations 16 and 17 appear from the same steps of derivation as in the previous paper but are supposed to represent (and look) something different. Here, an explanation of what is the key difference compared to previous work would help a lot (it probably requires very little but I can't really judge based on the information given). It should not be the job of a reader to spend an afternoon or two to re-assess the math and try to find out what is different. Even more importantly is the question to what degree the results are a fortuitous result of the reaction chosen.
3. Following up on that: I sometimes had a hard time understanding in what sense now the "equilibrium" assumption is to be understood. Why is a solution for the reaction rate needed (line 259) and its pre-requisites such as "solute disequilibrium" (eq. 7)? What is the meaning of the latter (also plotted in Fig 2(b)) if equilibrium is supposed to be applicable? Should the arguments in section 3.3 (but see criticism of that section in Point 5 below) come further up-front to make this clearer?
4. The manuscript would very much benefit if the "planar" flow results would also be visualized as the resulting fronts look different from the radial case, i.e., the aquifer can be heated up to the injection temperature for significant distances, displaying a true "front" rather than an outward migrating diffusive-looking profile.  
Then, for both cases it'd be then interesting if a minimal phenomenological description of the underlying physics would be provided why the progressing fronts have the shape that they have. I was a bit surprised that in the radial case it takes very long times to heat even the nearest region around the injection well to injection temperatures. Is that because the radial flow velocities slow

down rapidly with radial distance, enhancing conductive heat loss relative to the planar case?

5. I had a hard time understanding the logic in sections 3.3 and 3.4. First, in my understanding, the main argument on which the analysis rests is not provided but referenced to an appendix of the previous publication (line 410). Why not simply and up-front repeat the key point from there that the thermal front advancement and the reactive front coalescence is simply due to the timescale involved and the nature of the reaction?

Then, there is often unclear writing and wording. For example, what is, in simple words, meant with “thermal front end location”? To me, it sounds like the thermal front comes to a final halt. But then it appears that this is rather meant as the furthest distance of thermal perturbation due to injection at a given time (the outer end of the non-sharp front)? But then, the definition in line 404 and the following manipulations don’t seem convincing. First, there is not one position where the criterion is fulfilled but for a given  $\epsilon$  the condition is fulfilled for all  $r$  greater than a certain value (which I presume is this  $r_F$ ). Second, the choice of  $\epsilon$  would be arbitrary and, given the shape of the curve, potentially have a significant impact on the location of  $r_F$ . I strongly suggest re-writing this whole part in much simpler and more approachable form. Please try to put yourself into the position of the reader who has not done your work and wants to understand what you did.

Another example for strange wording is the “elongation” in section 3.4. Fronts advance and broaden but don’t “elongate”. So, it seems you mean advancement, which would be a more commonly used term? And certainly not broadening, right? Although in the radial case it is a mixture of both ... Also, as it is written (e.g., lines 443, 447), at least for me, it comes across as if  $x_F$  and  $r_F$  refer to the thermal and reactive fronts, respectively, while later it appears that these refer to the fronts in the planar and radial case. Please remove these ambiguities.

There are plenty more such examples in the whole text, so a general overhaul towards clarity is highly desirable.

6. Generally, figure captions are too long and often too unclear. Too long: they should not contain explanation that belongs in the text (e.g., Fig 4). Too unclear: e.g., again Fig. 4: why don’t you clearly state that panel (a) is for the planar and (b) for the radial case etc.? Or even put a respective label into the respective panels. Even with relatively careful reading it took me way too long to catch what “the low-flow-rate limit assuming conduction only” (panel C) should display. Most other figure captions show similar problems.
7. Very important: what is the relevance of the example calculations for real problems? Injection durations of 200, 10’000 and 100’000 years are unheard of and are very likely to be never implemented (for industrial-scale CO<sub>2</sub> storage currently 25 years are typical projections). When extrapolating the magnified part of Fig. 2(c) to shorter times, it seems that one might, for real problems, enter a region where the analytical equilibrium solutions fail to be good approximations. Please discuss this.
8. The “reactions” are simple solubility curves without any actual reaction (e.g., a pH and aqueous speciation in the calcite case is excluded). It’d be desirable to see some reflection how applicable the solutions might be in more complex cases with multiple species and temperature dependencies of equilibrium constants that are less favorable for “coalescence” than in the calcite case. Nature has

examples with multiple reaction fronts progressing at different velocities (contact metamorphic aureoles, skarns in marble layers cross-cut by hydrothermal veins etc.), so these obviously didn't "coalesce" with the thermal front.

To me, this makes the stated applicability to hydrothermal ore deposits questionable (where the author explicitly states: "A particularly intriguing phenomenon, often primarily controlled by the dependence of solubility on temperature, is the zoning of metals and minerals, which is commonly observed at various field scales. In these cases, regular belts of different precipitants form progressively as the distance from the hydrothermal fluid source increases." – so, how does this match the result of the present study with a single such precipitation front aligning with the thermal front being a key outcome?).

This is particularly the case for porphyry copper deposits where the author seems to be not on top of the discussion. Already in 1992, Hemley and Hunt (*Econ. Geol.*, 87, 23-43) specifically eluded on the role of precipitation fronts and their dependence on transport, heat transfer rates etc. Also, the geometry and hydrology of porphyry systems (e.g., Weis et al., *Science*, 2012) does not compare well with the problem studied here. Interestingly, in porphyry copper deposits, there are transport-limited reaction fronts, seen as alteration halo as these have been studied well (e.g., Cathles and Shannon, *EPSL*, 2007).

For such reasons, I strongly suggest leaving out much of the rather speculative discussion related to natural examples in its current form. Rather provide some that clearly relate to the problem studied in the sense of Fig. 1 or not mention them.

In spite of this criticism, I found the work quite inspiring. The more it seems important to make it more approachable and clear such that people can benefit from it.