Author Response to Reviewer #2's Comments

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Below, I provide detailed responses to all comments (quoted verbatim in bold).

> **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:**

I am grateful to the Reviewer for his careful review and for the important and constructive comments. The detailed conceptual and technical feedback is highly appreciated and will significantly contribute to improving the manuscript and enhancing its clarity. Below are the responses to the comments and the corresponding plan for the intended revisions.

Reviewer's Comment (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 m3 per second, they were taken as 500 m3 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.**

I thank the Reviewer for catching this important typographic error in the table (the in-text value in the previous work and in Fig. 4 of the current manuscript correctly indicate the intended values).

Summary of proposed revisions:

- Table 1 will be corrected in the revised manuscript.
- A corrigendum will be submitted to HESS for the previous publication.

Reviewer's Comment (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.**

I fully agree with the Reviewer that the distinction from the prior work should be made clearer. To both highlight the contribution of the current study and avoid repetition, I propose relocating most of Section 2 ('Settings and Model Equations') to an appendix, while revising the main Section 2 to focus more directly on the elements relevant to the present work. This restructuring will reduce redundancy in the main text while keeping the full model description readily accessible to readers.

Specifically, the *"Supplement to Responses to Referee 2"*, which outlines the derivation of the equilibrium model, appears at the end of this document. This short derivation will comprise the main focus of the revised Section 2. I believe this adjustment, based on the attached supplement, helps clarify how the simplifying equilibrium assumption is implemented and how it differs from the framework established in the previous work.

Furthermore, with respect to the similarity to the previous study, it is noted that—had it not been for the time gap—this study and Roded et al. (2024) could have been published together as companion papers. Since this was not the case, and in order to provide the necessary background and ensure the manuscript stands on its own, some repetition of the model settings and equations has been included, though direct text duplication was avoided. Additionally, Section 3.2.1 ('Comparison to the Reference Solution') provides brief background information to facilitate the comparison between the results of the newly developed solutions and those of the previous work (the 'reference solutions'). I am also open to making changes to Fig. 1; however, this figure simply outlines the Reactive Lauwerier Problem (RLP) and cites the source of the previous open-access study.

Summary of proposed revisions:

- Relocate substantial portions of Section 2 to an Appendix, while revising the main body of Section 2 to focus on the key equations and aspects directly relevant to the current study.
- Revise the analytical derivations for clarity and show the logic of the approach, and how it specifically differs from the derivations presented in the previous paper.

Reviewer's Comment (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?**

I thank the Reviewer for pointing out that these issues were not made clear. I believe that the proposed revision of Section 2—outlined at the end of this document under the heading *"Supplement to Responses to Referee 2"*—will help clarify these points.

Moreover, the manuscript will be revised to explain:

- Under the equilibrium assumption, the solution is derived for the reaction rate, $\Omega(\xi, t)$ where $\xi = r$ or x, rather than for the solute disequilibrium (or concentration). This is because the equilibrium model renders the inclusion of detailed kinetics unnecessary.
- For high Damköhler conditions and fast kinetics, quasi-equilibrium prevails, and $\Lambda \ll \Delta c_s$, where Δc_s denotes the absolute solubility change in the system ($\Delta c_s = |c_s(T_{in}) - c_s(T_0)|$)|, that is, between $c_s(T_{in})$ at the injection point to $c_s(T_0)$ at ambient conditions). Thus, solute disequilibrium is used to quantify the extent to which equilibrium holds across space and time (see Figs. 2b and 3a). Specifically, even within an equilibrium-assumption framework, it is useful to evaluate the

> disequilibrium, $\Lambda(\xi, t)$, to assess model applicability—particularly near the injection well, where deviations from equilibrium may emerge. The disequilibrium-based solution (Eq. B.3 of Appendix B) also serves in developing the applicability criterion for the equilibrium approximation, as presented in Section 3.3.

Lastly, following the proposed revisions intended to improve clarity, it may be preferable to retain the current order of presentation—beginning with the results in Figs. 2 and 3, followed by the derivation of the applicability criterion in Section 3.3—as this sequence appears to offer a clear and logical progression.

Reviewer's Comment (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 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?**

I agree that including the planar case in the results could be valuable. While the primary focus has been on the radial case, due to its greater relevance to geothermal systems and natural settings, the planar configuration is also of interest.

The Reviewer is correct in noting that, in the planar case, the aquifer can be heated over significantly greater distances. Regarding the difference in thermal front characteristics, the velocity decay in radial geometry indeed enhances conductive heat loss relative to the planar case. Specifically, in radial flow, the fluid velocity decreases with distance from the injection point, which leads to longer residence times and increased opportunity for heat to dissipate into the surrounding rock.

An additional contributing factor is the difference in heat conduction geometry. In the radial case, the heat source is effectively a vertical line (e.g., an injection well), with hot fluid spreading outward in all directions. In contrast, the planar configuration can be conceptualized as injection from a distributed source—such as a row of wells—generating a nearly uniform planar front. This planar setup facilitates more efficient heat retention and results in a front that advances farther downstream. Of course, in both cases, the thermal front behavior is also influenced by flow rates and the volume of injected hot fluid.

While this is not the central focus of the current work and may have been addressed in previous studies (e.g., Chen & Reddell, 1983; Stauffer et al., 2014; Ziagos & Blackwell, 1986), it is discussed in Section 3.4 (‘Development of Coalesced Fronts’).

In that section, the the thermal front outer-end (i.e., the furthest distance of thermal perturbation) is denoted as $\xi_F = r_F$ or x_F for the radial and planar cases, respectively. Specifically, it is identified as the downstream point where the temperature slightly deviates from the ambient, using the relation $\varepsilon = (T(\xi_F)-T_0)/\Delta T$. Here, ε is a prescribed small value ($\varepsilon \ll 1$) and $\Delta T = T_{in} - T_0$ is the temperature difference between injected and ambient fluids. Equations 29 and Fig. 4 present the evolution of r_F and x_F and illustrate the difference between the two cases.

Specifically, the *advancement rate* of the thermal front outer-end (i.e., $\partial\xi_F/\partial t$) decays significantly faster in the radial case: the derivative of the front location scales as $t^{-3/4}$, whereas in the planar case it follows $t^{-1/2}$. This analytical result highlights the fundamental physical difference in front propagation between the two geometries.

Summary of proposed revisions:

- Add results for the planar case to the supplementary material, similar to those presented in Fig. 2.
- Update Fig. 3 to include the planar case, illustrating the system’s state evolution over time and the applicability of the equilibrium solution (by duplicating the current insets for the planar configuration).

Note: These revisions may be further adjusted based on the Reviewer's feedback.

Reviewer’s Comment (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 font**

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 ϵ the condition is fulfilled for all r greater than a certain value (which I presume is this rF). Second, the choice of ϵ would be arbitrary and, given the shape of the curve, potentially have a significant impact on the location of rF. 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, is comes across as if xF and rF 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.

I thank the reviewer for raising these critical points, and I will carefully revise Sections 3.3 and 3.4 to improve clarity and make the content more accessible.

Regarding the main argument of the analysis: the first paragraph of Section 3.3 will be revised to more clearly and explicitly present the central reasoning. Specifically, it will emphasize that the coalescence of the reactive front and the thermal front is governed by the timescales involved and high Damköhler number conditions. The coalesced fronts then migrate in response to the thermal field evolution. With respect to the reference to the appendix of the previous publication in line 410, it is intended only to cite the specific equation used in the analysis, not to support the main conceptual argument.

Concerning the definition of ε in line 404 (i.e., $\varepsilon = (T(r_F) - T_0)/\Delta T$, where $\varepsilon \ll 1$), I will revise the text to explicitly state that ε refers to a specific, prescribed small value (here taken as $\varepsilon = 0.01$) that is used consistently in the analysis and substituted into Eqs. 11 and 18. For a given prescribed value of ε (and hence of a), the definition of r_F in Eq. 23 becomes unique.

While the choice of ε—restricted to values where $\varepsilon \ll 1$—is somewhat arbitrary, the resulting expressions (Eqs. 26 and 27) remain valid and unaffected. Furthermore, the results shown in Fig. 4a and 4b, which are based on Eqs. 29, are not expected to change appreciably depending on the exact choice of ε. This section will be rewritten in a clearer and more accessible form to ensure these points are clearly communicated.

I will also revise the terminology and replace the word “elongation” throughout Section 3.4 with “advancement,” which more accurately reflects the intended meaning. Additionally, the ambiguity surrounding the definition of the front outer-end position variables—x_F and r_F, in the planar and radial cases, respectively—will be addressed by clearly and consistently defining these terms upon their first mention.

Reviewer’s Comment (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.**

Figure captions throughout the manuscript will be shortened and revised to enhance clarity. Specifically, I fully agree with the Reviewer that panel (c) of Fig. 4, which refers to the low-flow-rate limit, along with its associated text, is unclear and will be carefully revised to improve clarity.

Reviewer’s Comment (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 CO2 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.**

I thank the Reviewer for these important comments. The manuscript will be revised to emphasize that the modeled scenario is not limited to engineered injection settings but is also relevant to natural systems (as noted in lines 132–133 of Section 2.1.1), where flow and reactions can occur over geological timescales. Additionally, the manuscript will be updated to include simulation results for a 25-year duration in Fig. 2 (replacing the current 200-year curve).

As the Reviewer correctly notes, at earlier times, the system is more likely to enter a regime in which the assumptions of the analytical equilibrium model break down—particularly near the injection point—as also indicated by the applicability criterion derived in Eq. 26. The manuscript will be updated to explicitly discuss these limitations of the equilibrium solutions in the context of applied geothermal and hydrological systems.

Reviewer's Comment (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 reactions 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.

Due to the simplifications required to derive closed-form expressions, analytical solutions typically apply directly only to a narrow set of real-world cases—if at all. However, they are valuable for establishing fundamental conceptual understanding, identifying key functional relationships, and also serving as important benchmark cases for validating numerical models (which are more useful for exploring real-world scenarios).

I thank the Reviewer for noting in detail that the scenario considered in this study is, however, too simplified to support extrapolated conclusions regarding ore deposit formation.

With respect to the applicability of the solutions to more complex cases—such as those involving multiple species and temperature-dependent equilibrium constants less favorable to coalescence—this applicability is limited. I believe that such systems cannot be adequately captured using the current equilibrium-approximated solutions. However, I am considering whether the set of equations for solute disequilibrium, such as B.1 or B.3 (Appendix B), can be implemented in a semi-analytical, coupled and iterative manner. This approach could potentially represent solutions for a multi-species system operating far from equilibrium, as these equations account for first-order reaction kinetics.

Similarly, under quasi-equilibrium conditions, it may be feasible to employ the equations presented in Eq. 16 or 20 in a semi-analytical, coupled form to model multi-species behavior. Nonetheless, the validity of such an approach remain subject to further evaluation.

Furthermore, the development of more advanced solution frameworks that incorporate additional kinetic and thermodynamic couplings remains a direction for future work. This outlook, along with its associated challenges, will be briefly discussed in the revised manuscript.

Summary of proposed revisions:

- Excluding the discussion related to ore-formation.
- Add a discussion outlining possible pathways for extending the solutions presented in this work and the previous study to more complex kinetic systems and to account for additional or more intricate inter-couplings.

Final Reviewer's Comment:

> **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.**

I once again thank the Reviewer for the careful review, insightful and important comments, and positive attitude. This will certainly help improve the manuscript and enhance its clarity and accessibility for a broader readership.

Supplement to Responses to Referee 2: Outline of the Derivation of the Equilibrium Model

Assuming the reactive Lauwerier problem settings and starting from the stationary, radial solute advection–reaction equation in the aquifer:

$$0 = -u\frac{\partial c}{\partial r} - \Omega(r,t), \tag{S.1}$$

where r is the radial coordinate, u is the Darcy flux, c is the solute concentration [M L^{-3}] and $\Omega(r, t)$ is the reaction rate, which varies in space and time, t (Chaudhuri et al., 2013; Szymczak and Ladd, 2012).

Defining the solute disequilibrium, Λ, as the difference between the dissolved ion concentration, c, and the temperature-dependent solubility (i.e., saturation concentration), $c_s(T)$,

$$\Lambda = c - c_s(T), \tag{S.2}$$

Equation S.1 can then be rewritten as:

$$0 = -u\left[\frac{\partial \Lambda}{\partial r} + \frac{\partial c_s}{\partial r}\right] - \Omega(r,t). \tag{S.3}$$

Next, assume high Damköhler number conditions and that the reaction kinetics are fast compared to the advective transport rate. Under these conditions, quasi-equilibrium prevails, and the solute disequilibrium satisfies, $\Lambda \ll \Delta c_s$, where Δc_s denotes the absolute solubility change in the system, $\Delta c_s = |c_s(T_{in}) - c_s(T_0)|$, i.e., between $c_s(T_{in})$ at the injection point to $c_s(T_0)$ at ambient conditions. Under these conditions, the first advective term ($-u\partial\Lambda/\partial r$) becomes negligible compared to the other terms, and Eq. S.3 can be approximated as (Andre and Rajaram, 2005; Phillips, 2009, see p. 237):

$$\Omega(r,t) = u\frac{\partial c_s(T)}{\partial r}. \tag{S.4}$$

Given an expression for $c_s(T)$ (e.g., Eq. 8 in the main text) and a defined temperature field (e.g., the Lauwerier solution in Eq. 11), a closed-form expression for the reaction rate $\Omega(r, t)$ can be obtained. Notably, this solution for $\Omega(r, t)$ is independent of the specific reaction kinetics involved.

Last, given the solution to Eq. S.4 for the reaction rate, the change in aquifer porosity, θ, can be calculated by solving:

$$\frac{\partial\theta}{\partial t} = -\frac{\Omega(r,t)}{\nu c_{\mathrm{sol}}}, \qquad (S.5)$$

where c_{sol} is the concentration of soluble solid mineral and ν accounts for the stoichiometry of the reaction.

Remark 1: The previous work focused on solving the full form of Eq. S.1 (or equivalently, Eq. S.3) without invoking the local equilibrium assumption. In contrast, the current approach solves the reduced form given in Eq. S.4.

Remark 2: The solution for the planar case can be obtained by following the same steps outlined above.

References

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