

## Author Response to Reviewer #1's Comments

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

- **This is a well-written manuscript that presents simplified, equilibrium-based solutions to the Reactive Lauwerier Problem, which models how thermal changes drive mineral reactions in subsurface aquifers. By assuming reactions are fast compared to fluid transport (i.e., a high Damköhler number), the author derives clear analytical solutions for how porosity and reaction rates evolve. These are shown to agree well with more detailed kinetic models, except very close to the injection point. The paper offers a useful criterion for when the equilibrium assumption is valid and applies the findings to real-world processes like CO<sub>2</sub> injection, silica precipitation, and ore formation. The work builds on previous studies and contributes useful insights. I recommend publication after minor clarifications, particularly around what's new compared to the earlier work (Roded et al., 2024b) and how to interpret the model's limitations near injection wells.**

I thank the Reviewer for the thoughtful review and the constructive comments, which are greatly appreciated. The suggestions provided will contribute meaningfully to improving the clarity and structure of the manuscript. Below, I provide detailed responses to each of the Reviewer's comments, along with a description of the planned revisions to the manuscript.

1. **Clarifying the Contribution of the Work:** In line with the Reviewer's comment, and consistent with feedback from Referee #2, the manuscript will be revised to more explicitly differentiate the present study from the earlier work (Roded et al., 2024). To make this distinction clearer, Section 2 ('Settings and Model Equations') will be restructured: most of its current content will be relocated to an appendix, while the main Section 2 will be revised to focus more directly on the derivation and implications specific to the equilibrium model developed in this study. To support this restructuring, a supplementary note—titled "*Supplement to Responses to Referee 1*" and included at the end of this document—has been prepared. This note outlines the derivation of the equilibrium model and will form the core of the revised Section 2.

**2. Model Limitations Near Injection Well:** I thank the Reviewer for highlighting the important issue of model limitations near the injection well, where the local equilibrium assumption may break down—a point that was also touched on by Referee #2. The manuscript will be revised accordingly. Under high Damköhler number conditions and quasi-equilibrium assumptions, deviations between the equilibrium and kinetic solutions are generally confined to a narrow zone near the injection point (see Fig. 2c). However, in dissolution-dominated cases, these localized deviations may still be significant (see lines 334–341).

Moreover, at very early times or under conditions farther from equilibrium (i.e., lower Damköhler numbers), the system is more likely to transition into a regime where the assumptions of the analytical equilibrium model no longer hold—particularly near the inlet. This breakdown is illustrated in Fig. 3a and is also captured by the applicability criterion derived in Section 3.2.3 (Eq. 26). This consideration is particularly important in practical geothermal and hydrological contexts, where projection times typically span only several decades. The revised manuscript will explicitly address these limitations of the equilibrium model and clarify its domain of applicability.

## Supplement to Responses to Referee 1: 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:

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

where  $r$  is the radial coordinate,  $u$  is the Darcy flux,  $c$  is the solute concentration [ $\text{M L}^{-3}$ ] 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,  $\Lambda$ , as the difference between the dissolved ion concentration,  $c$ , and the temperature-dependent solubility (i.e., saturation concentration),  $c_s(T)$ ,

$$\Lambda = c - c_s(T), \quad (S.2)$$

Equation S.1 can then be rewritten as:

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

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  $\Delta c_s$  denotes the absolute solubility change in the system,  $\Delta c_s = |c_s(T_{\text{in}}) - c_s(T_0)|$ , i.e., between  $c_s(T_{\text{in}})$  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):

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

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,  $\theta$ , can be calculated by solving:

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

where  $c_{\text{sol}}$  is the concentration of soluble solid mineral and  $\nu$  accounts for the stoichiometry of the reaction.

**Remark 1:** The solution for the planar case can be obtained by following the same steps outlined above.

**Remark 2:** 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.

## References

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Roded, R., Aharonov, E., Szymczak, P., Veveakis, M., Lazar, B., and Dalton, L. E.: Solutions and case studies for thermally driven reactive transport and porosity evolution in geothermal systems (reactive Lauwerier problem), *Hydrol. Earth Syst. Sci.*, 28, 4559–4576, 2024.

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