Response Statement to Referee's Comments (RC3)

Wang and Jeng

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The authors thank the reviewer for the valuable comments. The manuscript has been revised by carefully considering all the comments. The changes are highlighted in the marked copy, and detailed responses to the reviewer's comments are provided below.

General Comment:

The work addresses a well-recognized gap in reactive transport modelling: the integration of mechanical deformation with multicomponent geochemistry. The manuscript is generally well written and logically organized, and it fits well within the scope of coupled processes in hydrology and earth sciences.

Response (General Comment):

We thank the reviewer for the positive and encouraging assessment of our work. We appreciate the recognition that the manuscript addresses a well-recognised gap in reactive transport modelling by integrating mechanical deformation with multicomponent geochemistry, and that it aligns well with the scope of coupled-process studies in hydrology and earth sciences.

We have carefully reviewed the manuscript and implemented targeted revisions to further clarify the coupling framework and to improve the overall clarity and organisation of the presentation, while maintaining a clear focus on the physical and chemical mechanisms underlying the proposed model.

Comment #RC3-1:

It would be helpful to more explicitly articulate what new capabilities are enabled here beyond coupling OpenFOAM with PhreeqcRM. For example, a short comparison paragraph contrasting this framework with TOUGHREACT or COMSOL approaches would clarify this.

Response:

We thank the reviewer for this helpful suggestion. We have added a short comparison paragraph clarifying that, beyond a technical coupling of OpenFOAM and PhreeqcRM, the proposed framework enables equation-level formulation and control of fully coupled hydro–mechanical–chemical processes, in which mechanical deformation is explicitly represented as one of the driving mechanisms influencing reactive transport.

[Added new content:] *While established platforms such as TOUGHREACT and multiphysics implementations in COMSOL provide comprehensive tools for reactive transport modelling, they are not specifically developed to investigate deformation-driven reactive transport in near-saturated, deformable porous media within a unified continuum-mechanics framework. The strength of the present framework lies in its research-oriented numerical architecture, which allows the governing equations, coupling structure, and solution strategy of hydro–mechanical–chemical processes to be explicitly formulated and systematically controlled at the equation level. This capability is central to investigating deformation-driven reactive transport in near-saturated deformable porous media, which is the focus of this study.*

[Line 258–259]

Comment #RC3-2:

The assumption of constant saturation (which may not be true in vadose zones) is central to several conclusions. I wonder what the physical interpretation of "near-saturated" is and how sensitive the results are to small variations in saturation.

Response:

Thank you for this insightful comment. We agree that the assumption of constant saturation requires careful physical interpretation, particularly in vadose-zone settings.

In the revised manuscript, we clarify that "near-saturated" conditions refer to a regime in which the liquid phase forms a continuous network that governs flow, while the gas phase is present only as isolated, immobile bubbles that do not participate in advective transport. Under these conditions, saturation may be treated as approximately constant, and the influence of residual gas is primarily reflected through its contribution to the effective compressibility of the pore fluid–solid skeleton. This justifies the adoption of a single-phase liquid formulation within the specified range of applicability.

We have also explicitly stated the limitations of this assumption, noting that it becomes inappropriate when significant drying, strong transient infiltration, or connected gas pathways develop, in which case a fully unsaturated multiphase formulation would be required.

With respect to sensitivity, additional analyses within the tested saturation range (S_r = 0.8–1.0) indicate that variations in saturation significantly affect the magnitude and rate of hydro-mechanical responses, such as excess pore pressure dissipation and stabilisation time, while the ultimate mechanical deformation (final settlement) remains relatively insensitive. In contrast, the chemical response exhibits higher sensitivity: decreasing saturation leads to increased aqueous solute concentrations and an expanded plume extent, associated with changes in advective transport intensity and effective aqueous volume. Importantly, although saturation influences response magnitudes, the governing mechanisms and comparative trends remain consistent across the investigated saturation range.

[Added new content:] *The porous medium is assumed to remain nearly saturated. The liquid phase forms a continuous network and controls flow, while the gas phase is idealised as isolated, immobile bubbles that do not participate in advection. Hence, the degree of saturation S_r is prescribed as a constant rather than solved as a state variable, leading to a single-phase liquid formulation in which residual gas influences the system only through the effective compressibility of the pore fluid–solid skeleton. This treatment is consistent with mass conservation under drained conditions, whereby the decrease in pore volume during consolidation is accommodated by outward Darcy drainage, so that the volumetric water content $\theta = nS_r$ evolves implicitly through the liquid-phase mass balance while S_r is treated as approximately constant. This approximation is suitable for wet, low-permeability geomaterials where S_r typically exceeds 0.8–0.9 and varies slowly relative to the consolidation timescale, such that deformation-driven transport dominates over transient unsaturated flow, as in compacted clay barriers and landfill liners under quasi-steady infiltration.*

The formulation becomes invalid when drying fronts develop, when strong transient infiltration induces significant saturation changes, or when connected gas pathways form such that gas-phase transport is no longer negligible. Under these circumstances, prescribing S_r is inappropriate and the single-phase assumption may fail (Zeng et al., 2011). Accordingly, the present modelling philosophy is to focus on deformation-driven transport under quasi-saturated conditions, rather than adopting thermodynamics-based unsaturated multi-field frameworks in which saturation, multiphase pore pressures and chemical potentials are fully coupled (Liu et al., 2025). This simplification is appropriate for a wide range of low-permeability geomaterials under near-saturated conditions, in which saturation evolves slowly relative to the consolidation timescale and gas connectivity remains limited, so that deformation-driven transport dominates over transient unsaturated flow processes.

[Line 258–259]

[Deleted content:] ~~Overall, these results confirm that the solute and acidity peaks spatially align with the sources of the contaminant.~~

[Added new content:] *Overall, the results indicate that saturation variations exert a stronger control on chemical concentrations and plume geometry than on the final mechanical deformation. Although saturation influences*

response magnitudes, the governing mechanisms and comparative trends remain consistent across S_r 0.8-1.0.

[Line 258–259]

[Deleted content:] ~~Saturation strongly influences both the hydro-mechanical response and the reactive-solute distribution.~~

[Added new content:] *Saturation plays a key role in both hydro-mechanical responses and reactive-solute transport, with a more pronounced influence on chemical concentrations and plume evolution.*

[Line 258–259]

Comment #RC3-3:

The manuscript excludes reaction-induced changes in porosity and permeability. The authors should more clearly discuss how this assumption may bias long-term predictions.

Response:

Thank you for this insightful comment. In the revised manuscript, we have expanded the discussion to more clearly explain how neglecting reaction-induced porosity and permeability evolution may influence long-term predictions.

Specifically, we now clarify that excluding these feedback mechanisms may lead to a systematic bias towards smoother flow fields and less heterogeneous concentration distributions in reactive environments. Reaction-driven changes in pore structure, such as mineral dissolution or precipitation, are known to locally modify permeability and porosity, potentially enhancing preferential flow pathways and amplifying plume irregularity over long time scales. By neglecting these effects, the present framework may therefore underestimate the degree of spatial variability and channelling in long-term solute transport.

Accordingly, the model results should be interpreted as providing conservative estimates of plume spreading and migration patterns under reactive conditions. This limitation, together with its implications for long-term predictions, is now explicitly discussed in the revised manuscript.

[Added new content:] *For long-term conditions involving large settlements, plastic deformation of soft clays, or pronounced geochemical alteration, a more comprehensive framework would be required, incorporating elasto-plastic or visco-plastic constitutive behaviour together with reaction-driven porosity–permeability feedbacks. These processes are expected to intensify preferential flow pathways and enhance solute plume heterogeneity, such that neglecting them may lead to smoother transport patterns and an underestimation of plume spreading in reactive environments. Future work will focus on integrating these feedbacks and on quantitative benchmarking against laboratory and field observations to further strengthen the predictive capability of the framework.*

[Line 258–259]

Comment #RC3-4:

The treatment of molecular diffusion uses a weighted-average diffusion coefficient. I wonder how these weights are selected in practice.

Response:

The weighting factors ω_i are not arbitrarily selected. They are obtained from the initial geochemical speciation calculations and represent the relative fractions of aqueous species at the start of the simulations. In the present implementation, these fractions are prescribed as constant parameters for clarity and reproducibility. The effective molecular diffusion coefficient is then evaluated as a weighted average of species-specific diffusion coefficients retrieved from the PHREEQC database. A clarification has been added to the manuscript to make this procedure explicit.

[Added new content:] *Within the coupled hydro–mechanical–chemical framework adopted in this study, the relative fractions of aqueous species ω_i, obtained from the initial geochemical speciation calculations, are prescribed as constant parameters.*

[Line 258–259]

References

Liu, J.H., Ma, T.S., Fu, J.H., Gao, J.J., Martyushev, D.A., Ranjith, P.G., 2025. Thermodynamics-based unsaturated hydro-mechanical-chemical coupling model for wellbore stability analysis in chemically active gas formations. Journal of Rock Mechanics and Geotechnical Engineering 17, 3644–3661. doi:https://doi.org/10.1016/j.jrmge.2024.09.024.

Zeng, Y.J., Su, Z.B., Wan, L., Wen, J., 2011. Numerical analysis of air-water-heat flow in unsaturated soil: Is it necessary to consider airflow in land surface models? Journal of Geophysical Research: Atmospheres 116. doi:https://doi.org/10.1029/2011JD015835.