Preliminary Author Response to Anonymous Referee #2

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We sincerely thank the referee for the careful evaluation of our manuscript and for the positive assessment of the research topic, manuscript organization, and presentation of the results. We greatly appreciate the constructive comments, which identify several points where the physical interpretation, numerical formulation, and broader implications of the study can be clarified further. Below, we provide a preliminary point-by-point response to each comment. At the present interactive discussion stage, our responses focus primarily on the scientific issues raised by the referee and on how we intend to address them. Detailed changes to the manuscript, including the exact revised text and corresponding line numbers, will be implemented after the Editor provides the formal post-discussion decision and will then be documented systematically in the revised manuscript and the accompanying response letter. For clarity, the referee's comments are reproduced in black, followed by our preliminary responses in blue.

General comment

Wu et al. use pore-scale simulations to investigate how evolving aqueous chemistry, interfacial charge, electrolyte concentration, and pore architecture regulate transient electroosmotic transport in low-permeability porous media. The topic is interesting, the manuscript is generally well organized, and the figures clearly present the main results. However, several minor issues require further clarification before publication. My comments are listed below and I hope they will help the authors improve the manuscript.

Response

We sincerely thank the referee for the positive assessment of the research topic, manuscript organization, and presentation of the results. We also appreciate the constructive suggestions for further clarification. We address these comments individually below and believe that they will help improve the clarity and rigour of the manuscript.

Major comments

Major Comment 1: The model imposes a potential difference of 0.25 V across the computational domain while water electrolysis is treated as the only electrode reaction. Please clarify how the electrolysis flux is related to the imposed electrical potential and whether the 0.25 V represents only the transport domain voltage drop rather than the full electrode potential difference, particularly considering the thermodynamic potential required for water electrolysis.

Response 1

Thank you for raising this important point. We agree that the distinction between the imposed potential drop across the transport domain and the full electrochemical cell voltage should be clarified. In the present model, the imposed 0.25 V represents the electrical potential drop across the 2.5 mm electrode-to-electrode computational domain, including the 2.0 mm porous test section and the two 0.25 mm buffer zones, corresponding to a nominal electric-field strength of 100 V m^{-1}. It is not intended to represent the total electrode-to-electrode voltage required to drive water electrolysis.

Water electrolysis is represented as a current-coupled boundary source rather than through an explicit electrode-kinetic model. Specifically, the H^+ and OH^-, production fluxes are calculated from the normal ionic current density through Faraday's law, as described in Sect. S2. The imposed transport-domain potential therefore affects the electrolysis flux indirectly through its influence on the simulated ionic current density, while it is not used as an electrode overpotential or as a criterion for electrolysis onset. Thus, the imposed 0.25 V is not used to determine the thermodynamic onset or kinetic rate of water electrolysis; rather, electrolysis is prescribed as the electrode boundary process, with its production flux coupled to the ionic current. The standard electrode potentials reported for Reactions (R1) and (R2) are included to identify the corresponding water-electrolysis half-reactions and are not used to determine either the imposed transport-domain voltage or the electrolysis reaction rate in the present model. Equilibrium electrode potentials, activation overpotentials, and other electrode- or circuit-related voltage losses are not explicitly resolved in the present framework.

In the subsequent revision, we will clarify this distinction in the descriptions of the electrode reactions and electrical boundary conditions to avoid interpreting the imposed 0.25 V as the complete electrochemical cell voltage.

Major Comment 2: The model solves the Poisson equation for porewater charge density while the interfacial electric double layer is not explicitly resolved and electroosmosis is represented by a slip condition. The authors should clarify the consistency between these two treatments and demonstrate that the numerical resolution is sufficient for the charge-density and electric-potential fields under the tested electrolyte concentrations.

Response 2

Thank you for this important comment. We agree that the distinction between the resolved porewater electrostatic field and the unresolved interfacial electric double layer should be clarified. In the present formulation, Poisson's equation describes the electric potential and aqueous space charge associated with the explicitly transported ionic species in the resolved fluid domain. In

contrast, the interfacial double layer adjacent to the mineral surface is not spatially discretized; its electrokinetic effect is incorporated through the chemistry-dependent zeta potential and the Helmholtz–Smoluchowski slip condition. The interfacial charge variables used in the EDL/ETL closures are therefore not additionally introduced as volumetric charge or electrical body force in the resolved porewater domain.

The numerical mesh is consequently intended to resolve pore-scale bulk concentration and electric-field variations rather than the nanometre-scale diffuse layer itself. The same meshing and boundary-refinement strategy was applied across all electrolyte conditions. For the representative TT30 case, the existing mesh-convergence assessment shows very small M2–M3 differences in the resolved tangential electric-field components (relative L_2 differences below 0.004%), providing representative evidence for the numerical stability of the resolved bulk electric field. We do not interpret this representative test as an exhaustive concentration-by-concentration convergence demonstration of the aqueous charge-density field.

In the subsequent revision, we will make this scale separation and numerical interpretation more explicit. We will also clarify that the calculated porewater charge density represents resolved bulk aqueous space charge and should not be interpreted as a directly resolved diffuse-layer charge profile.

Major Comment 3: Group-level means and standard deviations are calculated across six deterministic pore geometries that include structurally different SROE, HD, and ND configurations. Please clarify the physical meaning of pooling these geometries and ensure that the resulting statistics are interpreted as descriptive summaries rather than measures of statistical uncertainty or ensemble behavior.

Response 3

Thank you for this important comment. We agree that the pooled means and standard deviations should be interpreted strictly as descriptive summaries across the tested deterministic pore geometries, rather than as measures of statistical uncertainty or ensemble variability.

The purpose of pooling the six geometries within each electrochemical group is to provide a compact summary of the overall range of structure-associated variation and to compare its magnitude with the larger between-group electrochemical contrasts. The geometries were not sampled as independent realizations from a common statistical population, and the reported standard deviations therefore do not represent sampling uncertainty.

This interpretation is already reflected in Table 3 and its note, but in the subsequent revision we will make it more explicit in the Results and figure captions and will consistently refer to these quantities as descriptive means and standard deviations across the tested deterministic geometries.

Major Comment 4: The Discussion could better emphasize the broader implications and limitations of the pore-scale findings. A stronger discussion of how the identified controls on transport magnitude, timescale, and plume organization may influence larger-scale electrokinetic transport and remediation systems would improve the significance of the manuscript.

Response 4

Thank you for this valuable comment. We agree that the broader implications of the pore-scale findings should be articulated more clearly. The present results suggest that larger-scale electrokinetic transport may not be adequately represented by a single, time-invariant electroosmotic mobility, because evolving aqueous chemistry can modify the available transport capacity, while pore structure redistributes that transport among different directions and pathways. The results also indicate that transport magnitude, transport timing, and plume organization should be distinguished when interpreting electrokinetic systems. For example, earlier attainment of a transport stage does not necessarily imply greater depletion at a later fixed time. These distinctions may be relevant when interpreting or parameterising larger-scale electrokinetic flushing and remediation systems.

At the same time, we agree that these implications should remain appropriately qualified. In the subsequent revision, we will strengthen the Discussion to connect the pore-scale mechanisms more explicitly to larger-scale behaviour, while emphasizing that quantitative upscaling will require three-dimensional or image-based structures, structural ensembles, more complete aqueous chemistry, and contaminant-specific transport and reaction processes.

Minor Comments

Minor Comment 1: Lines 135-145: Please report representative Reynolds numbers to support the stated low-Reynolds-number flow regime.

Response 1

Thank you for this suggestion. We agree that reporting representative Reynolds numbers would provide a more quantitative basis for the low-Reynolds-number assumption. In the subsequent revision, we will calculate and report representative *Re* values using the simulated porewater velocities, fluid properties, and a characteristic pore/grain length scale. We will also clarify that the resulting values remain well within the low-Reynolds-number regime, consistent with the negligible role of inertial effects in the present simulations.

Minor Comment 2: Lines 255-260: Please explain why the molecular diffusivity of Org was set equal to that of Cl^-, and provide supporting references if available.

Response 2

Thank you for this comment. In the present study, Org is an idealized neutral conservative tracer rather than a specific organic compound. Because no contaminant-specific molecular diffusivity is intended, we selected a fixed reference value of 2.03×10^{-9} m^2s^{-1}, equal to that used for Cl^-, to provide a consistent molecular-diffusion scale across all simulations without introducing an additional contaminant-specific parameter.

We agree that this modelling choice should be explained more clearly. In the subsequent revision, we will clarify that $D_{Org} = D_{Cl^-}$ is a controlled modelling assumption rather than a statement of chemical equivalence. No contaminant-specific reference is implied by this choice, and the resulting tracer behaviour should not be interpreted quantitatively for any particular organic contaminant.

Minor Comment 3: Line 264: Please provide a brief physical justification or supporting references for selecting 30 min as the common simulation window.

Response 3

Thank you for this comment. The 30 min simulation duration was selected as a common comparison window that is long enough to capture the early displacement, intermediate redistribution, and late-time persistence of the tracer across the different electrochemical conditions, while maintaining the same physical observation period for all 24 cases.

We agree that this rationale should be stated more explicitly. In the subsequent revision, we will clarify that the 30 min duration is a comparative modelling window rather than a universally representative treatment time, and that threshold times not reached within this interval are treated as right-censored.

Minor Comment 4: Lines 265-270: Numerical convergence is mainly demonstrated using TT30; please clarify whether similar numerical behavior is expected for the more extreme TH cases.

Response 4

Thank you for this comment. We agree that the convergence assessment based on TT30 should not be interpreted as a formal demonstration of mesh and time-step convergence for every TH case. TT30 was selected as a representative coupled case for the detailed discretization assessment, and the same meshing strategy, boundary refinement, solver formulation, and numerical settings were applied consistently across the full simulation matrix.

Although the TH cases involve the highest electrolyte concentration, they generally exhibit weaker electroosmotic velocities and slower tracer displacement than TT, which does not suggest greater hydrodynamic resolution requirements. Nevertheless, the higher ionic strength may introduce additional electrochemical stiffness. In the subsequent revision, we will clarify that the TT30

analysis provides representative evidence of numerical convergence rather than an exhaustive case-by-case proof, and will state this limitation more explicitly when discussing the TH results.

Minor Comment 5: Lines 278-285: Please discuss whether the periodic upper and lower boundaries affect transverse flow and plume displacement in the rotated geometries.

Response 5

Thank you for this important comment. The periodic upper and lower boundaries were used to represent a laterally repeating porous domain and to avoid introducing artificial side-wall constraints that could suppress transverse flow in the rotated geometries. Under these conditions, fluid and solute crossing one transverse boundary re-enter through the opposite boundary, so the boundaries do not act as sources or sinks.

We agree, however, that this assumption affects how transverse plume displacement should be interpreted. The reported transverse flow and plume reorientation therefore represent geometry-induced directional redistribution within a periodic representative domain, rather than displacement against impermeable lateral walls. In the subsequent revision, we will clarify this physical interpretation and the associated limitation in the boundary-condition description and Discussion.

Minor Comment 6: Lines 320-329: The 15-30 min interval used to define the tailing index requires further justification, and a brief justification or sensitivity statement would be useful.

Response 6

Thank you for this helpful comment. The 15–30 min interval was selected as the latter half of the common 30 min simulation window to provide a consistent measure of late-window tracer persistence across all cases. It is intended as a comparative persistence metric rather than as a universal definition of the onset of tailing.

We agree that this rationale should be stated more explicitly. In the subsequent revision, we will clarify the purpose of this interval and emphasize that TI_{CMZ} is interpreted together with the complementary fixed-time depletion and threshold-time metrics, rather than as a standalone measure of transport performance.

Minor Comment 7: Lines 345-350: Please indicate whether this temporal mismatch has a measurable effect on the plume descriptors.

Response 7

Thank you for this comment. The interpolated stage-attainment time and the stored concentration field used for plume analysis can differ by at most 0.025 min because the model-output interval is

0.05 min. This provides a strict bound on the temporal mismatch introduced by the nearest-output extraction procedure.

A separate sensitivity analysis of the plume descriptors to this temporal offset was not performed. In the subsequent revision, we will explicitly report the maximum mismatch and clarify that the reported plume descriptors inherit the 0.05 min temporal resolution of the stored concentration fields. We will therefore avoid implying a higher temporal precision than that supported by the saved-output interval.

Minor Comment 8: Lines 370-379: Please clarify the sensitivity of the concentration-ridge results to the selected smoothing, peak-height, prominence, and separation criteria.

Response 8

Thank you for this important comment. We agree that the detected number and spacing of concentration ridges can depend on the smoothing and peak-detection criteria, particularly for marginal local maxima. In the present analysis, a single fixed set of smoothing, peak-height, prominence, and minimum-separation criteria was applied consistently to all Scenario II cases and progress stages to provide a uniform supplementary diagnostic.

We therefore do not interpret the detected ridges as parameter-independent geometric features. Importantly, multiple ridges were identified in only 2 of the 24 analysed profiles, and the ridge analysis was not used to establish the main transport rankings or a general HD–ND channelization contrast. In the subsequent revision, we will clarify this parameter dependence and further emphasize the supplementary and qualitative role of this analysis.

Minor Comment 9: Lines 540 to 548: HD reaches the 90 percent depletion threshold earlier than ND under TO and TT but shows lower depletion after 30 min. A brief explanation of this apparent difference between threshold attainment time and end window depletion would help readers interpret these metrics.

Response 9

Thank you for pointing out this apparent contrast. The two metrics characterize different aspects of the transient response. $t_{90,\mathrm{CMZ}}$ records the first time at which the normalized CMZ concentration falls to 0.10, whereas $\eta_{30,\mathrm{CMZ}}$ describes the depletion state at the fixed observation time of 30 min.

Thus, under TO and TT, HD reaches the 90% depletion threshold earlier, but the subsequent depletion trajectories of HD and ND differ such that ND ultimately reaches a lower residual CMZ concentration and hence greater CMZ depletion at 30 min. We will add a brief explanation of this

distinction in the Results to make clear that earlier threshold attainment does not necessarily imply greater end-window depletion.