

Reply to reviewer #2

We thank the reviewer for finding our work interesting and for identifying its relevance to the HESS readership. The comments from the reviewer were seminal in improving our work and mainly in putting it in the right context. These comments also allowed us to implement the simulation results in the main text while commenting on the level of similarity between them and also commented and compared the various electric potentials for various distances in the Nernst-Planck equation. We are extremely grateful to the reviewer for the time invested in reviewing our work. We believe that we have responded (marked in blue) to all the comments by the reviewers (marked in black).

The manuscript provides very interesting experiments and interpretations. However, it requires revision before publication in HESS for the following reasons:

- It should contain a state of the art of the reactive transport experiments already performed in the past and better highlight the contribution of this paper (see for example additional paper listed below and references here in).

We are grateful to the reviewer for providing these references on the Nernst-Planck implementation and validity for flow in porous media. While this is not the main focus of the paper, it is an important aspect in establishing all the contributing factors to the pH migration in our experiments. We have incorporated these references in the introduction and in section 3.2.3.

See lines:

“Specifically for pH reactions, experimental data with high Peclet value for transverse reaction are in good agreement with the Advection-Dispersion-Reaction equation (ADRE), which uses a single diffusion coefficient for all species in a multispecies reactive system \cite{Lawniczak}, especially in stirred flow-cell reactors \cite{Liu2011}”

And

“Simulations performed on experimental results from a Hele-Shaw cell (\cite{Huang 2023, Almarcha 2010}), showed the importance of considering the Coulombic interaction via the Nernst-Planck equation and species specific diffusion coefficient for density-driven flow in bulk. Additional simulations and experiments on porous media, coupling the electrical gradient with various flow configurations, while considering the different diffusion values for each reactive species, yet for high Peclet, pointed to the important role of Coulombic interactions during reactive transport \cite{rolle2018nernst,rolle2013coulombic}, yet it remains to be seen how relevant it is to the system presented in this study.”

- The supplementary material should be included in the manuscript. The processes considered in the modelling should be detailed. Parameters, boundary conditions, space and time discretizations for the simulation of the flow and the transport should be given and justified. The differences between the model and the experimental data should be commented in

details.

Not including the simulation section within the main manuscript is an overlook on our part, and we have moved it to the main manuscript from the supplementary. Moreover, following the reviewer's comment, we added a section to the methods focused on the simulation details (section 2.3). In this section, we describe the simulation type, grid size, equations, and 2D comparison between the model and the results are now stated. The difference between the experimental results and the simulation is now reported in section 3.4. While these simulations do provide the descriptive model for the R6G and pH migration, we are of the opinion that the simulations are not seminal for the main finding in the paper.

"2.3 Comsol simulations

The results for both the mixing and reactive experiments, described in section 2.1, were simulated using the Comsol multi-physics Stokes flow simulator. To that end, the Autocad file with the 2D design and dimensions of the flow cells was imported to the simulator with their dimensions and no slip and no flow boundary condition for the pillars and walls. The inlet and outlet were defined as a Dirichlet boundary condition, corresponding to the constant flux condition imposed by the syringe pump. The simulation followed the following laminar flow equations for an incompressible fluid, namely the continuity, mass conservation, and viscous stress, respectively:

$$\rho \frac{\partial u}{\partial t} + \rho(u \cdot \nabla)u = \nabla \cdot [-pI + K] \quad (10a)$$

$$\rho \cdot u = 0 \quad (10b)$$

$$K = \mu(\nabla u + (\nabla u)^T) \quad (10c)$$

Where ρ is the fluid density, u is the velocity in vector form (marked by bold) aligned and transverse (T) to the principal flow direction, ∇p is the pressure drop over the determinant I, K is the stress tensor, and μ is the fluid viscosity. To account for the transport of the R6G and basified solution, the following transport equation is used to account for the concentration (C_n) of specific chemical species noted by n:

$$\frac{\partial c_n}{\partial t} + \nabla \cdot J_n + u \cdot \nabla c_n = R_n \quad (11a)$$

$$J_n = -D_n \nabla c_n \quad (11b)$$

Where J_n is the diffusive flux calculated for each chemical species by its corresponding diffusion coefficient, D_n , and the chemical retardation factor per species R_n . The concentration, C_n , is inserted as mol/M3 at the inlets according to the experimental values and as a fixed boundary value.

The maximum and minimum element sizes within the adaptive mesh used for the solid boundaries in the simulation are 1070 and 49.3 μM , while the maximum and minimum element sizes for the fluid calculation are 101 and 4.5 μM , for the adaptive mesh in the finite element linearized calculation. The simulation begins with the introduction of either the R6G or pH difference at the two inlets simultaneously, and allowing the simulation to evolve up to the initial time frame in the experiment stated in section 2.1, namely 5 and 10 minutes for the Darcy velocity of 1.42, and 0.142 mm/s, respectively, while the time discretization ranging between 5 to 15 seconds depending on the level of heterogeneity. The study state flow is achieved extremely fast within the simulation (1 ~ 2 simulated minutes), and therefore, there was no need to run it for another 5 and 10 minutes as in the experiment. These mesh sizes and temporal discretization were optimized to get the best results under the best stability, and

simulations took about 5 minutes on a Core i5, 10 Gen computer with 16 Gig of memory. For each iteration, the concentration, velocity, and pressure were extracted, while the simulated 2D spatial distribution for the R6G and pH were compared with the experimental values using the 2D R2 function in Matlab.”

– The concentration normalization assumes a linear relationship between intensity and concentration (eq. 5). Please comment.

We thank the reviewer for providing us the opportunity to clarify this point. As stated in section 2.2.1, the normalization of the R6G concentration is based on the Beer-Lambert law that linearly relates the intensity with the concentration. As stated at the end of that paragraph, this relation was also verified in other studies but also experimentally verified for our setup by saturating the flow cell with DDW with a known concentration quantity of R6G and imaging it through the microscope.

– What is the reliability of an experiment, i.e., what is the difference in the transverse missing/dispersion when repeating a reactive transport experiment?

The reviewer is right, and the reliability analysis reported in response to reviewer 1 comment did not separate between the R6G and the pyranine pH measurements. In fact, the same analysis is done for the R6G, and for the pH experiments, recall that the intensity value is used to infer both R6G concentration and pH value. That is why we reported it in 2.2 and not in the specific subsection for mixing and reactive experiments. We now corrected this issue by clarifying in the text that this test was done for both experiments:

“As such, this intensity analysis, which provides both the error bounds and repeatability of the layout, is done for both the R6G and pH experiment.”

– I do not understand why the distance between the two inlets is used for the computation of the ion fluxes due to non-neutral electric field generated by differences in the diffusion coefficients (Nernst-Planck equation). This gradient should be a local one (not at the scale of the setup), that can be computed using the images. Please clarify and comment.

This is an interesting point raised by the reviewer, and it refers to the calculation of both the diffusion component in the Nernst-Planck equation and the Coulombic interaction, as shown in Rolle et al 2017. As such, the Δx term is used for both the concentration difference for the diffusion and for the electric field derived from the electrostatic potential. Therefore, changing this value for one term will similarly change the second term, leaving the ratio between them the same. As such, we are not sure this will change the overall effect. Then again, it could very well be that we misunderstood the reviewer’s comment, and if so, we humbly ask for some more clarification.

Minor comments:

What is the pixel size of the images?

The magnification used for these experiments is 2X (now stated in section 2.2), and therefore each pixel is a $3.3 \times 3.3 \mu\text{M}$ per pixel. We added this to the manuscript:
“All experimental images taken by the confocal are taken by a Prime BSI camera with a 95 % quantum efficiency and $1e^-$ median noise, with an exposure time of 500 ms, bit depth of 16-bit, and magnification of 2x, providing a resolution of $3.3 \times 3.3 \mu\text{M}$ per pixel”

What is the reliability of the concentration values (0.1 % camera noise but what about the uncertainty related to the calibration)?

The uncertainty of the calibration is done by the same uncertainty measurement done for the image analysis stated in section 2.2:

“For the 100 $\mu\text{L/h}$ flow rate, a series of 50 pictures were taken 5 minutes after forming a stable interface between the fluids. Then, after an additional 5 minutes of delay, another series of 50 pictures is taken, under the same conditions. The two series of images are compared to verify the stability of the interface. For the 10 $\mu\text{L/h}$ flow rate, the same imaging sequence was performed, with an initial time of 10 minutes and a subsequent delay time of 10 minutes. For both flow rates, the variance of each pixel intensity (marked as I_{ij} , for location ij) for the 50 picture sequences taken for each time, did not exceed 1%. To verify that the interface among image sequences for different times is stable, the criteria were set that the difference between the initial and later imaging sequence that exceeded the 0.1% (white noise of the camera) was averaged in absolute terms, and the stability of the interface was established if the average difference was isotropic and smaller than 1% (namely, $\langle \frac{|I_{ij}(t=5) - I_{ij}(t=10)|}{|I_{ij}(t=10)|} \rangle > 0.1\% < 1\%$) a similar analysis was performed around the interface to verify that the 1% difference is not the outcome of the bulk behavior.”

Please check units through the document and use SI format.

Done

L108: “simultaneous” -> “simultaneous”

Done

L269: “relay” -> “rely”

Done

L133: a character space is missing “solution(Barzan and Hajiesmaeilbaigi, 2018)”.

Done

Same for L140, L194.

Done

Two “=” in equation (8) which should be (9).

Done

References

Huang et al., 2023, doi.org/10.5194/gmd-16-4767-2023

Loyaux-Lawniczak S. et al. (2012) DOI: 10.1016/j.jconhyd.2012.06.005

Rolle et al., 2013. doi.org/10.1016/j.gca.2013.06.031

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Rolle et al., 2018, doi.org/10.1002/2017WR022344