

List of manuscript updates:

The manuscript was transformed into latex.

1. Abstract

The abstract is unified into one paragraph.

2. Introduction

The introduction was shortened to balance the general reactive transport process and the specific pH-induced reaction, which are the topics of this study. Specifically, lines 25 and 35-40 were extracted (shown below) while their references were moved.

“It is important for the understanding of numerous Earth Sciences problems ranging from engineering applications such as carbon capture and storage or groundwater remediation, as well as geological studies, to watershed or global issues(Carrera et al., 2022).”

“At the macroscale, the advection-dispersion reaction equation (ADRE) is usually used to describe reactive transport. However, it may provide incorrect predictions of experimental results in reactive systems, including the extent of reactions in mixing-controlled chemical transformations (Battiato and Tartakovsky, 2011; Berkowitz et al., 2016). This is mainly because the ADRE is not sensitive to incomplete mixing at the pore scale, in which biogeochemical reactions occur(Edery et al., 2013, 2009; Alhashmi et al., 2015).”

A section on ADRE approaches for capturing reactive transport phenomenon for pH reactions, and additional references are added in line 40:

“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 (Loyaux-Lawniczak et al. (2012)), especially in stirred flow-cell reactors (Liu et al. (2011)). ”

A summary of the plan for the article was added, starting in line 54 (now line 43) with a sentence that marks the need for the experiments we performed, followed by a summary of the rationale behind them. See the following paragraph:

“Considering the coupling between mixing and reactive transport processes and how both are scaled with the heterogeneity, specifically in the context of pH reactions in heterogenous soil, a set of experiments is proposed to observe if, indeed, the same coupling between mixing and reaction occurs for pH spread and reactions. These experiments focus on investigating how porous medium layouts ranging from homogeneous to heterogeneous affect pH-driven reactions by examining the pattern of transverse dispersion of co-flowing fluids for both mixing and pH. This is done by tracking the mixing and pH spread for two Peclet values using fluorescently labeled fluids imaged by a confocal microscope. The mixing experiments showed that transverse mixing varies from diffusive mixing in the homogeneous case to shear-driven mixing in the heterogeneous case. However, the pH measured in the pH experiments does

not follow the pH value calculated from the mixing pattern. Instead, it shows a larger spread, suggesting that the co-flowing fluids' pH difference equilibrates faster than the mixing. We identify the proton transfer mechanism, which is comparatively faster than the transverse dispersion or diffusion, as the dominant mechanism, especially for lower Peclet. Pore-scale simulations agreed well with the mixing experiments and provided reasonable results for the pH experiments after considering the enhanced diffusion due to the proton transfer mechanism.”

Furthermore, spaces were added to the references and grouped into one parathesis.

3. 2.1. Experimental methods

Missing experimental details on the syringe pump, syringe type, fluid characteristics, temperature, etc., were added. Effective diffusion, linking the change in diffusion with the heterogeneity by scaling the diffusion with the tortuosity and porosity and how that changes the Peclet, was added. A table summarizing these parameters was also added. See below.

“Each cell had two parallel inlets (right and left), each of them set at 425 μm from the edge of the cell, and one funnel shaped outlet. At the two outlets, a syringe pump (Chemyx Fusion 200 Two Channel model) with a small diameter glass syringe (100 μL Hamilton glass syringe) allowed a continuous movement for the motor and the piston with no oscillations for the applied fluxes (100, and 10 $\mu\text{L}/\text{h}$ flow rate, resulting in a Darcy velocity of $v_d = 0.142$, and 0.0142 cm/s , respectively). These two velocities provided two Peclet numbers (Pe), as depicted by the following equation:

$$Pe = \frac{v_d R}{D} \quad (1)$$

The Peclet number is a measure of the velocity magnitude (v_d), and the diffusion (D), which is an intrinsic property of the fluids over the mean pore size (R) (Bossis and Brady (1987)). While the mean pore size remains the same for all heterogeneity, there are small porosity (ϕ) variations (see Table 1 for details). However, the main heterogeneity effect is on the interface between the co-flowing fluids, forming a torturous path. To address this, we define an effective diffusion coefficient $D_{eff} = \frac{D\phi}{T}$, which scales the diffusion of the reactants in water, as shown in many studies (Ray et al. (2018); Fogler (2011); Guo et al. (2022); Kim et al. (1987); Quintard (1993); Quintard and Whitaker (1993); Beyhaghi and Pillai (2011)). The tortuosity (T) can be directly calculated from the normalized standard deviation σ/R , which marks the range for the pillar center movement from a uniform grid using the following relation, $T = 1 + \sigma/R$, and leading to the effective Pe number of:

$$Pe_{eff} = \frac{v_d R T}{D\phi} \quad (2)$$

and scaling the Peclet number as depicted in Table 1.

The fluorescent conservative tracer used for the mixing experiments (Figure 1.a.) is rhodamine 6G (R6G), which is widely used to visualize flow patterns, such as in the domain of environmental hydraulics (Barzan and Hajiesmaeilbaigi (2018)). Pyranine (8-hydroxypyrene-1,3,6-trisulfonate) is used for the reactive and combined experiments (Figure 1.b.-c.) as the pH reactant, as its fluorescent emission spectra and intensity are highly dependent on medium pH (Avnir and Barenholz (2005)), therefore suitable for monitoring pH changes. The R6G's concentrations were 2 $\text{mg}/50 \text{ ml}$ double distilled water (DDW with $\approx 18 \text{ M}\Omega \cdot \text{cm}^{-1}$ at 25 $^\circ\text{C}$, the lab temperature, purified by Milli-Q) for the R6G (corresponding to 0.083 mM) and 9 $\text{mg}/50 \text{ ml}$

DDW for the pyranine (corresponding to 0.347 mM). These concentrations had no measurable effect on the fluid viscosity and density in this experimental setup.”

σ/R [-]	0.0	0.01	0.1	0.5
ϕ [-]	0.68	0.64	0.64	0.62
T [-]	1	1.01	1.1	1.5
Pe_{eff}/Pe [-]	1.47	1.58	1.72	2.42

Table 1. The table depicts the porosity, tortuosity, and effective Peclet ratio for each heterogeneity.

The terms “pH reactant”, “tracer”, and “background solution” were replaced to “acidified pyranine” and “basified pyranine” to mark the pH reactive components, “R6G” and “basified DDW” to mark the tracer experiments in the text and figures. The units were transformed to SI format in the text and the figures.

Figure 1.

The inlet fluid order is now aligned with the experimentally reported inlet fluid order. Furthermore, the curves in 1.e. were reduced to the pH range reported in this study and presented on a logarithmic scale to provide a better separation between the low and high pH curves, while an inset with a linear scale was added to provide the separation among the high pH curves. The curve textures were altered to provide a classification that can be identified by color-blind readers. The caption and color scheme reflect the change in the terms reported previously.

2.2. Imaging setup

The imaging setup section and image analysis section were merged and the numbering was updated. Details on the model microscope, camera, time frame, etc., were added, as well as an explanation of the criteria for establishing image quality within the sequence:

“For both the R6G and reactive experiments, a confocal microscope (Nikon Eclipse Ti2-FP) was used to visualize the intensity change due to the mixing and reaction within the flow cell. The R6G is excited by a 546 nm laser, and tracked with the emission wavelength of 600 nm, while the pyranine is excited by a 405 nm laser and tracked with the emission wavelength of 550 nm. 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 x2.

For the 100 $\mu\text{L}/\text{h}$ 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 $\mu\text{L}/\text{h}$ 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, each pixel intensity (marked as I_{ij} , for location ij) at each 50 pictures sequence, the variance of intensity per pixel did not exceed the 0.1% white noise of the camera. To verify that the interface among image sequences is stable, the criteria was 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. Similarly, a program is developed to convert the image intensity received in the reactive experiments to its pH values. 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.”

2.2.1 Imaging the mixing experiments

The equation relating the concentration with the pH, and the accompanied text was added to the section:

“The change in local normalized concentration (C_{ij}) for the R6G and DDW mixing can be transformed to pH and compared to the acidified and basified pyranine mixing. As the pyranine emission amplitude changes with the OH^- groups, we base the calculation of pH on the OH^- migration. This is done by the equation below:

$$pH_{calculated} = -(14 - \log[C_{ij} \cdot 10^{-(14-low\ pH)} + (1 - C_{ij}) \cdot 10^{-(14-high\ pH)}]) \quad (8)$$

where low pH and high pH are the pH values of the acidified and basified pyranine solution.”

2.3 Comsol simulations

A section on the comsol simulation methodology was added:

“ 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:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}]$$

$$\rho \cdot \mathbf{u} = 0$$

$$\mathbf{K} = \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$$

Where ρ is the fluid density, \mathbf{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 , \mathbf{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 :

$$\frac{\partial c_n}{\partial t} + \nabla \cdot \mathbf{J}_n + \mathbf{u} \nabla \cdot \mathbf{c}_n = R_n$$

$$\mathbf{J}_n = -D_n \nabla c_n$$

Where \mathbf{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/M^3 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 R^2 function in Matlab.”

3.1 Mixing experiments

Figure 3.2 was combined with figure 4, and is now figure 4.b, the appropriate text in section 3.1 was moved to section 3.2 while the equation was moved to section 2.2.1.

3.2 Reactive experiments

The pH change analysis was re-written to reflect the terms of basified-acidified pyranine while characterizing the pH distribution through the symmetry and spread around the fluid interface:

“Examining the reaction pattern at a flow rate of 100 $\mu L/h$ in the more heterogeneous media, i.e., $\sigma/R = 0.1$ and 0.5 (Figure 4a.c.-d.), clearly shows that the interface between the two fluids is not symmetrically distributed around the middle of the cell. Rather, it tends to migrate leftwards as the flow proceeds, indicating that the reaction occurs earlier and closer to the area of the acidified pyranine (7.3). This interface migration due to the diffusive nature of the OH^- ions from high to low concentration occurs for all medium heterogeneities and was reported in previous studies on precipitation of $CaCO_3$ (Katz et al. (2011); Tartakovsky et al. (2007, 2008)), yet it becomes more dominant as the medium is more heterogeneous.”

The pH contrast coming from the experiments of R6G mixing is marked as a synthetic result by the term calculated pH and compared with Figure 4:

“The calculated pH at 10 $\mu\text{L}/\text{h}$ flow rate (Figures 4b.e.-h.) predicts a somewhat asymmetrical pattern regarding the basified vs. acidified pyranine distribution, and a slightly narrowing strip of the basified pyranine as fluids move towards the outlet zone, indicating that the reaction theoretically gets larger due to R6G diffusion. This increase is the outcome of the logarithmic scale of pH (see (8)), where the molar value of the access OH^- ion are orders of magnitude higher on one side, which dominates over the cross-section. However, reactive experiments show that basified pyranine moves vertically along the cell significantly more than the calculated pH predicts, and the volume of the basified pyranine is increased at the expense of the acidified pyranine. This demonstrates that the reaction does not necessarily follow the mixing pattern in porous media, as the pH spreads faster than the R6G concentration predicts, an aspect that has a clearer representation in the following section.”

The logarithmic nature of equation 8 which we use to transform the R6G concentration to pH, that leads to a sharper transition of the pH is now stated in the text:

“This sharp interface in pH value is probably due to the pyranine intensity exponential decay (2), and the logarithmic scale at which concentration is transforming to pH in (8).”

The sensitivity of the pH migration to the initial conditions at for the pH experiment is added:

“This substantial migration of pH towards the acidified solution (recall that the pyranine concentration is uniform throughout the cell, and only the pH differs) cannot be the outcome of the initialization of solutions in the flow cell, as these measurements were taken after 100 and 20 pore-volumes for the 100 and 10 $\mu\text{L}/\text{h}$ flow rates, respectively.”

3.2.1 Comparing the average pH transverse migration

Figure 5 was combined with figure 4, and is now figure 4.c. which allows a better comparison between the measured and calculated pH in figures 4.a and 4.b with their averaged product in figure 4.c.

The sharp transition of the measured and calculated pH is now discussed in terms of symmetry and spread:

“In each section, we calculated the average pH of each column of the matrix along the x-axis. The plotted results, shown in Figures 4c.a.-h., clearly show how the transition in pH has a sharp interface for both the calculated and measured pH, even when averaged spatially; yet they also emphasize that while the calculated pH is symmetric around the cell center, the experimental pH is very non-symmetrical and deviates significantly from the cell center, and this deviation between the calculated and experimental pH is worsened as the flow rate decreases.”

3.2.2 The role of diffusion in pH transverse migration

The results of the scaled Pe and transverse pH migration due to the enhanced diffusion of the pH are analyzed through the mean square displacement (MSD), and a table summarizing these calculations is added:

“This high diffusion rate leads to a diffusion dominated transverse flux captured by the pH enhanced spread as the applied flux reduces, forming a low Pe over the pore size. Calculating the OH^- transverse migration from the diffusion mean square displacement over the 10 s it takes for the fluid to advance the length of the cell (4.5 mm) for the 10 $\mu\text{L/h}$ flow rate (recall that the $v_d = 0.0142 \text{ cm/s}$), the high diffusion advances the OH^- 0.2 mm. As diffusion is isotropic in nature, it not only occurs transversely to the flow but also aligned with the flow, leading to a steady state of OH^- neutralized by the lower pH and marked by the acidified pyranine, as seen in the homogeneous case (Figure 4c.e). Multiplying this diffusion advancement by the Pe ratio reported in Table 1, brings this diffusion spread to 0.3 mm (see Table 3), nearly covering the full extent of the cell, and similar to the spread in (Figure 4c.e). However, for the same extent of time and Darcy velocity, the high shear in the heterogeneous case further mixes the OH^- , leading to full homogenization of the pH in the flow cell (see Figure 4c.h, and 3). Yet, the same increase in shear between the homogeneous and the heterogeneous case for the high flux/Pe, produces a smaller relative effect on the OH^- migration (Figures 4c.a-d).”

σ/R [-]	0.0	0.01	0.1	0.5
v_d [mm/s]	0.146	0.155	0.155	0.162
MSD [mm]	0.2	0.19	0.19	0.19
$k \times 10^{-6}$ [mm ²]	69	40	34	13
$MSD \times Pe_{eff}/Pe$ [mm]	0.297	0.31	0.336	0.468

Table 3. The table depicts the Darcy velocity, MSD, and MSD scaled by the effective Peclet ratio for each heterogeneity.

3.2.3 Calculating the ion concentration contribution to transverse migration

Missing dimensions were added to $J_D(OH^-)$ and $J_E(OH^-)$, and the reference to J_D and J_E are now clarified in equation the equation of the ion flux J :

“We repeated this calculation for the hydroxide ions (OH^-), the protons (H^+), the Cl^- and the Na^+ , and for all cases, the diffusive flux (marked by the first term in (10) and scales with D_{OH^-} [cm²/s]) was two to three orders of magnitude greater than the electric flux (marked by the second term in (10) and is approximately $J_E(OH^-) \approx 2 \times 10^{-7}$ [mol/cm²·s]) due to the ion concentration, making them negligible for our study (see Bard and Faulkner (2001) for details).”

We also incorporated and referred to relevant literature on the Coulombic interaction captured by the Nernst-Planck equation:

“Simulations performed on experimental results from a Hele-Shaw cell (Huang et al. (2023); Almarcha et al. (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 Rolle et al. (2018, 2013), yet it remains to be seen how relevant it is to the system presented in this study. yet it remains to be seen how relevant it is to the system presented in this study.”

3.3 Simulating the tracer and reactive experiments

The simulation section was moved from the appendix to the main manuscript.

Furthermore, the R^2 range for the simulation is now reported in the caption.

4 Summary and Conclusion

The section was separated into summary and conclusions.