Review of the manuscript entitled “Experimental investigation of the interplay between transverse mixing and pH reaction in porous media” in the *HESS* journal

General comments

The article proposes a research topic consistent with the journal. The article focuses on the impact of pH on mixing in porous media, using microfluidics for process visualization. The experimental method chosen is appropriate to the objectives, however, the numerical calculations and simulations proposed deserve some adjustments to improve the discussion of the results and the conclusions of the study.

The quality of the language used in the manuscript is good, but the writing needs to be adjusted to make it easier to understand. Indeed, although most of the elements required for comprehension are given, the use of ambiguous terms and the choices made in the article structure make reading more complex. In addition, the supplementary material contains “scientific interpretations or findings that would go beyond the contents of the manuscript” contrary to the journal guidelines. Restructuration of the manuscript must be done to include these numerical results.

Specific comments

1. It would be beneficial to achieve a more balanced distribution of the introduction between the general topic of reactive transport and the specific mixing issue. Additionally, the reactive transport section is somewhat difficult to follow due to the frequent shifts in scale.
2. At the end of the introduction, conclusions from the observation of the results are presented. However, the reader expects a summary of the plan of the article. The actual presentation of the plan could be more detailed than in its present form.
3. The use of “pH reactant”, “tracer”, and “background solution” to designate the different solutions used in the experiments is confusing. It would be clearer for the reader to use only specific designations, such as “R6G”, “acidified pyranine”, “basified pyranine”, and “basified DDW”. This is also the case of the legend of the scheme in Figure 1a, which would then be homogenized with the legends 1b and 1c. In addition, the left and right sides explain from which side the tracer or the background solution is injected. However, this orientation is reversed in Figure 1 compared to the description in the text and the results. In the same way, the designation of “mixing” or “reactive” is confusing because there is mixing in all of these experiments. This could be replaced by “R6G and DDW mixing”, “acidified and basified pyranine mixing”, and “acidified pyranine and basified DDW mixing”.

4. Some information about the experimental setup is missing in Section 2.1: the syringe pump model, flow rate values, density and salinity of the solutions, and temperature. Flow rates are indicated later in Section 2.2, but mentioning them first would be more logical when presenting the setup.
5. Some information about the imaging is missing in Section 2.2: the model of the microscope and the timeframe for the captured image sequence. In addition, it is unclear if all the presented images were taken after waiting 5 or 10 minutes for the respective flow rates of 100 and 10 µL/h or from the second capture (at 10 or 20 minutes, respectively) or if a mean image was created. The authors refer to image sequence acquisition and two acquisition periods, but the images' quality and stability over time are never discussed in the presentation of the results.
6. There is a numbering problem with the subsection “Image Analysis”, which could be merged with section 2.2 as “image capture and analysis”. In addition, the following subparts could be renamed not following the “mixing” or “reactive” designation, but tracer type.
7. The calibration curve for pyranine is obtained at a constant concentration. In the experiments of acidified pyranine and basified DDW mixing, the authors refer to the dilution of pyranine to explain the difference in pH observed compared to the results obtained with the acidified and basified pyranine mixing. However, pyranine is injected from the left side, and from the pH values, no dilution is observed on the opposite side of the cell with pH at 12.3, only in the middle with a lower pH value and brighter red color. Did the authors consider different calibration curves from lower pyranine concentrations?
8. The equations (7), (8), and (9), as well as the features of COMSOL simulations should be presented in the Method section. It is unclear if concentration C_{ij} refers to pyranine of R6G value in equation (8), the equation to calculate the pH. The equation to obtain the electric field value should also be added. The reference to J_D and J_E should be clarified in equation (9), the equation of the ion flux J.
9. There is no pH contrast in the experiments of R6G mixing. Figure 3.2 comes from synthetic results. This should be clearly stated and since this figure has to be compared with Figure 4, it would be more logical to merge it with Figure 4 and not describe it in section 3.1, but in section 3.2 instead. In addition, the results obtained in Figure 3.2 are surprising. From the color scale, no intermediate pH is observed at the mixing boundary (no visible yellow or green transition). I hope the authors can comment on this.
10. All the results of mixing experiments involving pH contrast show alkaline invasion in the left half of the cell. I hope the authors can discuss this effect regarding the initialization procedure, which consists of saturating the cell first with the alkaline solution.
11. Line 219, the thickness and symmetry of the interface are discussed based on Figures 3.2 and 4. Aside from the fact that this part of the discussion is difficult to follow, the interface is more visible in Figure 5. I suggest some discussion reformulation based on this.

12. The average pH along the x-axis at three different sections of the cell of the experiment of acidified pyranine and basified DDW mixing could be added to Figure 5 and discussed in a separate subsection 3.4.
13. The solutions used in the experiments have different chemical compositions, thus certainly different salinities, viscosities, and densities, affecting flow and mixing. I hope the authors can provide the information and add some comments to the discussion.
14. I am surprised by the methodology of calculating a specific Péclet number for each species, rather than calculating effective diffusion coefficients to obtain the Péclet numbers of each solution. Comparing the effective diffusion coefficients would bring more value to the discussion when comparing the results from the experiments of acidified and basified pyranine mixing with acidified pyranine and basified DDW mixing.

Technical corrections

- The abstract is usually a single paragraph.
- There is a missing space in the text before the left parenthesis of all citations.
- Two citations in the same sentence should be grouped in the same parentheses (e.g., line 21).
- Line 27: the formulation “geological studies, to watershed or global issues” could be clarified.
- The units are not presented in the SI format (e.g., “µl” should be “µL”, “hr” should be “h”, “sec” should be “s”) and the fraction format should be avoided and replaced with the inline format.
- The captions of figures 3 to 5 could be shortened since medium heterogeneities are already labeled.
- Figure 1e: the curves cannot be distinguished based on the chosen colors in the legend, even for non-color-blinded readers.
- There is a numbering problem for the equation of the ion flux: (8) should be (9).
- Line 269: misspelled “relay” should be replaced by “rely”.
- Units are missing when presenting the ionic mobility and the electric field (line 300), then for $J_D(OH^-)$ and $J_E(OH^-)$.
- The guidelines recommend separating the summary from the conclusions.