Mixing-Limited Effective Reaction Rates in Porous Media: An Explicit Prediction from Pore-Scale Mixing

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Abstract

Two solutes can share the same volume of a porous medium and still barely react, because sharing a volume is not the same as mixing. As the flow carries them, it stretches each into thin filaments that interleave through the pore space, and reaction is confined to the narrow fronts where those filaments meet. A continuum model that simply multiplies the average concentrations ignores this and overpredicts the reaction whenever the chemistry is faster than the flow can mix. We quantify that overprediction and turn it into a usable correction. Averaging the bimolecular rate law leaves a term, the reactant cross-covariance, that the standard continuum rate discards; written as a segregation intensity, it measures how incompletely the reactants are mixed within an averaging volume. We follow that quantity with a balance in which the dispersive flow continually produces fresh reactant contact while diffusion erases it, and we close the balance with a single mixing time. The effective rate constant that results is the intrinsic constant divided by one plus a mixing Damköhler number, the ratio of the time to mix to the time to react. Taking the mixing time from lamellar theory, in which the flow thins the reactant interface until diffusion can complete the mixing, makes the correction an explicit function of the Péclet and Damköhler numbers, evaluable from field or column data without any pore-scale simulation. In the fast-reaction limit it recovers the exact mixing-controlled rate of De Simoni and co-workers, and it reproduces the slower-than-expected product growth recorded in the Gramling, Harvey, and Meigs visualization experiment.

Article Highlights

In a porous medium the two reactants are drawn into thin filaments that remain largely separated, so a Darcy-scale model that multiplies their average concentrations overestimates the reaction.

The overestimation reflects a competition between mixing and reaction, captured by a single mixing Damköhler number that sets the effective rate.

Lamellar mixing theory supplies the mixing time, so the correction depends only on the Péclet and Damköhler numbers and reproduces the exact De Simoni result and the Gramling experiment without pore-scale simulation.

Keywords Reactive transport, Mixing-limited reactions, Pore-scale mixing, Effective reaction rate, Damköhler number, Lamellar mixing

1. Introduction

Pore-scale and continuum models of reactive transport are used to predict a wide range of subsurface processes, including mineral dissolution and precipitation, contaminant degradation, and microbially mediated redox reactions in sediments and aquifers (Blunt et al. 2013; Dentz et al. 2011; de Anna et al. 2014). Most predictions at the field and laboratory scales are made at the continuum (Darcy) scale with an advection-dispersion-reaction equation (ADRE), in which the velocity variability of the pore network is folded into an effective dispersion coefficient and the reaction term is evaluated with the locally averaged concentrations (Whitaker 1999). This description is convenient and, for slow reactions, accurate. It nonetheless rests on a hidden assumption, that the reactants sharing an averaged volume are also mixed together at the molecular scale at which reaction occurs. When that assumption fails, the ADRE systematically overpredicts the amount of reaction (Gramling et al. 2002; Dentz et al. 2011), and the error can be large enough to invalidate the macroscopic model altogether (Battiato et al. 2009; Battiato and Tartakovsky 2011).

This failure reflects the difference between spreading and mixing (Kitanidis 1994; Dentz et al. 2011). Spreading is the stretching and distortion of a solute plume by the velocity differences between fast channels and slow pores, and it is the quantity that dispersion measures. Mixing, by contrast, is the actual bringing-together of the two reactants at the pore scale, which only diffusion can accomplish, across the interfaces that spreading creates. Two plumes can be drawn into thin, interleaved filaments that occupy the same averaging volume and overlap strongly in the averaged fields, yet remain in separate pores and touch only over a small area (Le Borgne et al. 2013). The visualization experiment of Gramling, Harvey, and Meigs (2002) showed this directly: an essentially instantaneous reaction between $CuSO_4$ and EDTA in a transparent sand pack produced far less product than a Darcy-scale model predicted, and the deficit came solely from incomplete pore-scale mixing rather than from any error in the chemistry. Later pore-scale experiments confirmed that the reaction is confined to the thin, migrating fronts between the reactants and is paced by the local mixing rate (de Anna et al. 2014; Bijeljic et al. 2013).

The lowering of the rate by incomplete mixing has a long history. Averaging a bimolecular rate law leaves a reactant cross-covariance, or segregation, term that reduces the effective rate constant, an effect quantified for spatially variable flows by Kapoor, Gelhar, and Miralles-Wilhelm (1997) and carried into the volume averaging of reactive transport by Porta and co-workers (Porta et al. 2012). The conditions under which the macroscopic model breaks down, and the boundary between the reaction-limited and mixing-limited regimes, were established by Battiato and co-workers from multiscale arguments (Battiato et al. 2009; Battiato and Tartakovsky 2011). In parallel, the pore-scale mixing that controls the correction has been described by lamellar theory, in which the flow stretches the reactant interface into thin sheets that diffusion then smooths (Le Borgne et al. 2013, 2015;

Villermaux 2019). What has been missing is a single, transparent expression that ties these threads together and gives the effective rate directly from quantities a modeler already has.

Incomplete mixing is known to lower the reaction rate, but two practical questions remain open: by how much, and can the reduction be predicted from quantities a modeler can estimate rather than measured for each case? We answer them by averaging the reaction rate over a representative volume and following the calculation through to a single formula in the Péclet and Damköhler numbers. We (i) obtain the mixing correction by averaging the reaction rate, which leaves a term measuring how incompletely the two reactants are mixed; (ii) derive a balance for that term, separating what the flow creates from what diffusion removes; (iii) close the balance with a single mixing time, which expresses the rate as a competition between mixing and reaction set by one Damköhler number; (iv) obtain that mixing time from the way the flow stretches the reactants into thin filaments; and (v) test the prediction against an exact analytical result and the Gramling experiment. The correction is intended for continuum reactive-transport models, and it applies wherever the chemistry is faster than pore-scale mixing, from mineral precipitation to microbially mediated redox reactions.

2. Pore-Scale Transport and Reaction

We start at the pore scale, in the water between the grains, where the flow carries the reactants through the channels of the network. The pore water moves with velocity $u(x,t)$, the same incompressible flow field a pore-scale simulation produces. It carries two reactants that combine in the reaction $A+B\rightarrow C$ to form a product. Each concentration c_i is carried by the flow, smoothed by diffusion, and changed by reaction, exactly as in any pore-scale transport simulation. It therefore obeys an advection-diffusion-reaction equation,

$$\frac{\partial c_i}{\partial t}+u\cdot\nabla c_i=D_m\nabla^2 c_i+r_i, \tag{1}$$

with molecular diffusion coefficient D_m, and the reaction rate set by the law of mass action,

$$r_A=r_B=-k\,c_A c_B,\quad r_C=+k\,c_A c_B, \tag{2}$$

Here k is the rate constant measured in the laboratory, where the reactants are well mixed. Everything that follows comes from one feature of this rate: it multiplies the two concentrations together. Because of that product, the rate depends on whether the two reactants actually sit in the same pore, not just on how much of each is present in a region on average. This is the crux of the problem, and it is why a continuum model, which sees only averages, can get the rate wrong.

To reach the continuum (Darcy) scale, where models actually run, we average over a small block of the medium, the representative elementary volume (REV) familiar from upscaling. The block holds many grains and pores but is small next to the whole domain. It has total volume V, of which the pore water fills V_f, so the porosity is $\varphi=V_f/V$. The average concentration is the mean over the pore water in the block,

$$\langle c_i \rangle \equiv \frac{1}{V_f} \int_{V_f} c_i \, dV \,, \tag{3}$$

and we write each pore-scale concentration as this block average plus the variation around it from pore to pore,

$$c_i = \langle c_i \rangle + c_i{}' , \langle c_i{}' \rangle = 0. \tag{4}$$

Splitting a field into an average plus its variation is standard in upscaling (Whitaker 1999), and the same split underlies stochastic models of reactive mixing (Kapoor et al. 1997). The point is simple: a continuum model keeps only the block average and throws away the pore-to-pore variation. The next section shows that this discarded variation is exactly what decides the reaction rate.

3. Volume Averaging and the Effective Reaction Rate

We now find the rate a continuum model should use. The model has only the block-average concentration of each reactant, so it forms the rate by multiplying the two averages. But the true rate is the product of the two concentrations at each point, and the average of a product is not the product of the averages. The two differ, and that difference is the error we are after. Substituting the average-plus-variation split into the rate and averaging gives an exact result: the product of the averages, plus one extra term,

$$\langle c_A c_B \rangle = \langle c_A \rangle \langle c_B \rangle + \langle c_A{}' c_B{}' \rangle . \tag{5}$$

so the average rate at which product forms is

$$\langle r_C \rangle = k \left(\langle c_A \rangle \langle c_B \rangle + \langle c_A{}' c_B{}' \rangle \right) = k \langle c_A \rangle \langle c_B \rangle \left(1 + \frac{\langle c_A{}' c_B{}' \rangle}{\langle c_A \rangle \langle c_B \rangle} \right). \tag{6}$$

The first term is what a continuum model already computes. The second term is the error it makes. That term is large when the two reactants vary together so as to overlap, and small when they do not, so it measures whether A and B actually occupy the same pores. In a porous medium they often do not. The flow draws each reactant into thin filaments, and where one reactant is plentiful the other is largely absent, so a surplus of A sits where there is a shortage of B. The extra term is then negative, and it lowers the rate. We collect its size into a single number between zero and one, the segregation intensity, which is simply the fraction of the rate lost to incomplete mixing,

$$I_s \equiv - \frac{\langle c_A{}' c_B{}' \rangle}{\langle c_A \rangle \langle c_B \rangle} \in [0,1], \tag{7}$$

With this number the average rate keeps the form a modeler expects, the rate constant times the two average concentrations, but the rate constant is reduced in proportion to the incomplete mixing,

$$\langle r_C \rangle = k_{eff} \langle c_A \rangle \langle c_B \rangle , k_{eff} = k (1 - I_s). \tag{8}$$

The number runs from zero to one, and its two ends are easy to read. It is zero when the reactants are perfectly mixed; then the effective rate constant is the laboratory value and the continuum model is exact. It is one when they are completely unmixed, sharing a block but never touching; then the effective rate constant is zero, and no product forms no matter how much of each is present. Everything now hinges on this one number, so the rest of the paper is about predicting it.

4. Production and Dissipation of Reactant Overlap

To predict it, we follow the quantity it is built from, the overlap between the two reactants, written $g \equiv \langle c_A' c_B' \rangle$, and we ask what raises it and what lowers it as the flow moves the reactants around. Subtracting the average equation from the pore-scale equation gives an equation for the pore-to-pore variation of each reactant, and combining those gives a balance for the overlap g,

$$\frac{\partial c_i'}{\partial t} + u \cdot \nabla c_i' + u' \cdot \nabla \langle c_i \rangle - \nabla \cdot \langle u' c_i' \rangle = D_m \nabla^2 c_i' + r_i' . \tag{9}$$

Forming this combination and averaging gives a balance that follows the overlap g as the mean flow carries it through the medium,

$$\frac{\partial g}{\partial t} + \langle u \rangle \cdot \nabla g = P - \varepsilon + R , \tag{10}$$

The left side is ordinary transport. The right side carries the physics, in three competing effects, a production term P, a dissipation term ε, and a reaction term R. We take them one at a time. The production term,

$$P = -\langle u' c_A' \rangle \cdot \nabla \langle c_B \rangle - \langle u' c_B' \rangle \cdot \nabla \langle c_A \rangle , \tag{11}$$

is the flow making fresh contact between the reactants. The same velocity differences that spread a plume in any transport simulation drag the two reactants past one another, so new contact is created at the pore scale all the time. The dissipation term,

$$\varepsilon = 2 D_m \langle \nabla c_A' \cdot \nabla c_B' \rangle \tag{12}$$

is the pore-scale mixing itself, the rate at which diffusion smooths the contrasts between the filaments and drives the overlap g toward zero. This is the step that controls the whole process, because the reactants are truly mixed only once diffusion has erased the contrasts across the thin filaments the flow keeps drawing out (Le Borgne et al. 2013, 2015). The reaction term,

$$R = \langle c_B' r_A' \rangle + \langle c_A' r_B' \rangle \tag{13}$$

is the reaction acting back on the mixing. Reaction consumes the reactants where they overlap, so it removes the overlap and makes the mixing look even worse. There is a catch: this balance cannot be solved as it stands, because each of its three terms depends on finer pore-scale detail than the balance itself carries. This is the familiar closure problem of mixing, and to get past it we need one simple, physically reasonable assumption (Dentz et al. 2011; Porta et al. 2012).

5. The Effective Rate and the Mixing Damköhler Number

The assumption is the natural one. We treat diffusion as removing the overlap at a steady pace, over a single mixing time τ_m,

$$\varepsilon \simeq \frac{|g|}{\tau_m}, \tag{14}$$

which defines τ_m as the time diffusion needs to mix the contents of a block. With this, the whole process becomes two steps in sequence, exactly like two resistances in series. The reactants must first be brought together, which takes the mixing time, and then react, which takes the reaction time. Whichever step is slower controls the rate, so the two times add, and the effective rate is

$$k_{eff} = \frac{k}{1 + k C_0 \tau_m} = \frac{k}{1 + Da_m}, Da_m \equiv \frac{\tau_m}{\tau_r} = k C_0 \tau_m. \tag{15}$$

Setting this equal to the earlier expression for the effective rate gives the segregation intensity directly,

$$I_s = \frac{Da_m}{1 + Da_m}. \tag{16}$$

and a single number now controls everything, the mixing Damköhler number Da_m, the ratio of the time to mix to the time to react. This is the same Damköhler number used throughout reactive transport, now built from a mixing time. When mixing is faster than reaction, the segregation is small, the effective rate is the laboratory rate, and a continuum model is reliable. When reaction is faster than mixing, the segregation is large, the effective rate drops far below the laboratory value, and the rate becomes

$$\langle r_C \rangle \to \frac{\langle c_A \rangle \langle c_B \rangle}{C_0 \tau_m}, \tag{17}$$

which contains no rate constant at all: the reaction can proceed only as fast as the flow delivers freshly mixed reactant. A model that keeps using the laboratory rate constant on the average concentrations therefore overpredicts the reaction, and the overprediction grows with the Damköhler number. This is the whole story but for one missing piece: we have not yet said what the mixing time is. That is the subject of the next section.

6. An Explicit Mixing Time from Lamellar Theory

The mixing time comes from a simple picture of how the flow mixes, the lamellar picture (Le Borgne et al. 2013, 2015; Villermaux 2019). As the flow stretches and folds the reactant bodies, the boundary between them is pulled into thin filaments, one reactant inside the other, just as a tracer is drawn into thin strands in a pore-scale simulation. A filament starts about as wide as a pore, l, and the flow keeps thinning it at a stretching rate γ. The thinning stops once diffusion can cross the filament as fast as stretching narrows it. The time diffusion needs to smooth the filament at that point is the classical result,

$$\tau_m \simeq \frac{1}{\gamma} \ln\left(Pe_l\right), Pe_l = \frac{\gamma l^2}{D_m}, \tag{18}$$

This time grows only as the logarithm of the local Péclet number, because stretching keeps sharpening the gradients almost as fast as diffusion smooths them. At the pore scale the stretching rate is set by how much the velocity changes across one pore, so the local Péclet number becomes the ordinary pore Péclet number, and

$$\tau_m \simeq \frac{l}{U} \ln(Pe) = \frac{l^2}{D_m} \frac{\ln(Pe)}{Pe}. \tag{19}$$

This form is right when the flow dominates. It must also be right when the flow stops, where there is no stretching and mixing is by diffusion alone, taking the time for diffusion to cross a pore. One simple expression covers both ends,

$$\tau_m = \frac{l^2}{D_m} \phi(Pe), \phi(Pe) = \frac{\ln(1+Pe)}{Pe} \tag{20}$$

It is flat at low Péclet number, where mixing is by diffusion, and falls at high Péclet number, where stretching speeds mixing up. Putting this mixing time into the mixing Damköhler number leaves the whole correction in terms of two numbers a modeler already computes from field or column data,

$$Pe = \frac{U l}{D_m}, Da = \frac{k C_0 l^2}{D_m}, \tag{21}$$

the Péclet number, which compares flow with diffusion, and the Damköhler number, which compares reaction with diffusion. Together they give the prediction we set out to find,

$$Da_m = \alpha\, Da\, \phi(Pe), \frac{k_{eff}}{k} = \frac{1}{1 + \alpha\, Da \dfrac{\ln(1+Pe)}{Pe}}, \tag{22}$$

where α is a number near one that absorbs the details of the pore-scale stretching. The line where the mixing Damköhler number equals one separates two regimes: below it mixing keeps up and the ordinary continuum model is fine, and above it mixing lags and the correction is needed. This is the same boundary Battiato and co-workers found by an independent route (Battiato et al. 2009; Battiato and Tartakovsky 2011); what we add is its exact place and the size of the overprediction beyond it.

7. Prediction and Validation

The effective-rate ratio is the result, a prediction with a single free number, the order-one constant α. Figure 1 shows how it behaves. In panel (a), as the mixing Damköhler number crosses one, the mixing falls behind and the effective rate drops below the laboratory value. In panel (b) the same prediction is plotted against the Péclet number for several reaction strengths: a faster flow thins the filaments sooner, so mixing keeps up and the laboratory rate returns. These curves are predictions, not fits to data, and we now test them.

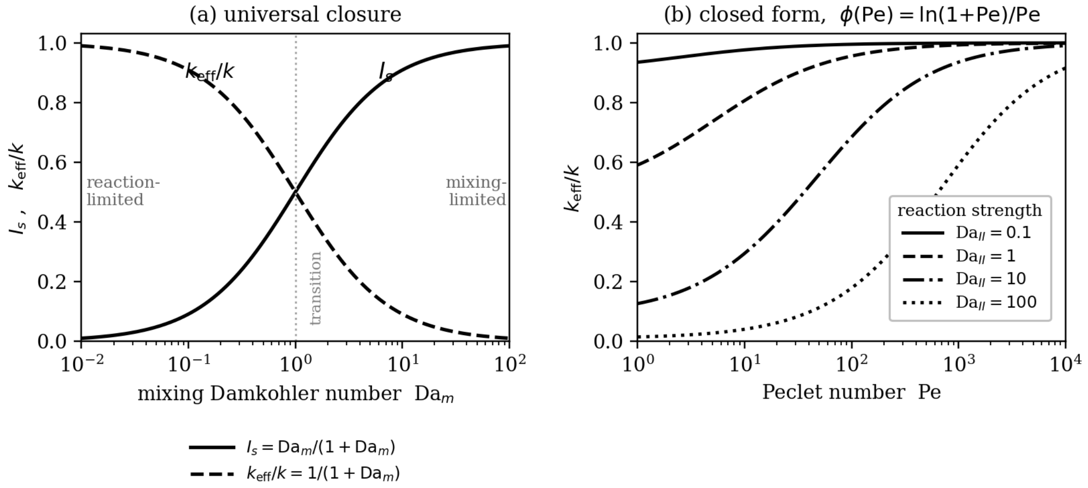

Figure 1. Predictions of the explicit expression. (a) The segregation intensity (solid) and the effective-rate ratio (dashed) against the mixing Damköhler number; the two regimes meet where that number equals one. (b) The effective-rate ratio against the Péclet number for Damköhler numbers $Da = 0.1, 1, 10, 100$ *(with* $\alpha = 1$*). A higher Péclet number speeds pore-scale mixing and restores the laboratory rate.*

We test the prediction in two independent ways, against an exact analytical limit and against a benchmark experiment.

Exact analytical limit. For an instantaneous reaction the mixing Damköhler number is large everywhere, and our expression gives a rate set entirely by mixing, not by chemistry. This is exactly the exact result of De Simoni and co-workers (2005), who showed that for an instantaneous reaction the local rate equals the pore-scale mixing rate of a conservative tracer times a fixed chemical factor. Our mixing rate is theirs, so in this limit our expression is not a new guess but a re-derivation of a known exact result.

Benchmark experiment. The Gramling, Harvey, and Meigs (2002) experiment is this instantaneous case: a very fast reaction between two reactant bodies set side by side in a uniform sand pack. Three of our predictions match what they measured. The product grows only as fast as the mixing front widens, not along the faster well-mixed curve, which is the slower growth they saw. The measured product stays below the Darcy-scale prediction, by exactly the factor the segregation removes, which here is far below one. And the gap widens as the reactants spread and the Damköhler number rises through the run.

These are agreements of trend and scaling, with no fitting beyond the single constant α; fixing α against the digitized product curve is the natural next step.

Quantitative check against the exact result. These two checks can be made into a number. In the Gramling setup the two equal-strength reactants meet at a sharp front and spread with the same coefficient, and for that case the method of De Simoni and co-workers (2005) gives the total product exactly, $M(t) = C_0\sqrt{(4Dt/\pi)}$, growing as the square root of time because the rate is set by the widening front, not by the chemistry. Our expression predicts the same law. Figure 2(a) compares it with a standard operator-split reactive-transport run of the same problem: the two agree to within 0.03 percent over more than two decades in time, both growing as the square root of time, as Gramling, Harvey, and Meigs (2002) measured. Figure 2(b) places the experiment on our universal curve, where the large Damköhler number puts the effective-rate ratio far below one, so a Darcy-scale model on the average concentrations overpredicts the product, just as the experiment found. The expression thus matches a published exact result to the digit and the experiment in its scaling.

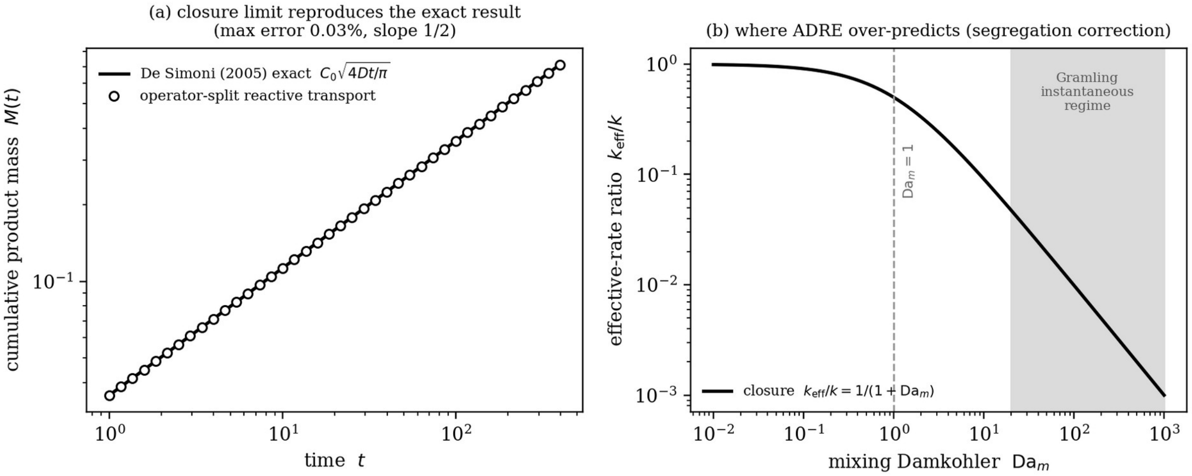

Figure 2. Validation against the exact result of De Simoni et al. (2005) in the Gramling et al. (2002) instantaneous-reaction setup. (a) Total product M(t) at a spreading front: the exact law $C_0\sqrt{(4Dt/\pi)}$ (line) and a standard operator-split reactive-transport run (markers) agree to within 0.03 percent, both growing as $\sqrt{t}$. (b) The same experiment on the universal curve: the Damköhler number is large (Da_m >> 1, shaded), the effective-rate ratio is far below one, and a Darcy-scale model on the average concentrations overpredicts the product, the gap the experiment reported.

8. Limiting Cases

Well-mixed batch. In a small, well-stirred volume there is nothing left to mix, so the mixing time is zero, the Damköhler number is zero, and the effective rate is the laboratory rate. For equal concentrations the averaged balance returns the textbook second-order rate law, so the framework contains ordinary, well-mixed kinetics as a special case.

Advection-dominated mixing front. When two reactants are carried past each other and meet at a front, the gradients are sharp, dispersion keeps feeding fresh reactant into a thin reactive layer, and diffusion across the stretched front sets the mixing time through the lamellar expression. As the reaction gets faster the front cannot keep up, the Damköhler number grows, and the product falls below the Darcy-scale prediction by the segregation factor, just as the pore-scale measurements of de Anna and co-workers (2014) show.

Steady transverse mixing zone. When two reactants are injected side by side and flow together, a reactive zone forms along their shared boundary, its width set by transverse dispersion. When reaction is fast, the product made per unit length is governed by how fast the two mix across that boundary and barely depends on the rate constant, so the effective rate is again the mixing rate, in line with the analysis of Cirpka and Valocchi (2007). The same expression thus covers a moving front and a steady zone alike, with only the mixing time changing between them.

9. Discussion

The result is useful because it makes the rate correction computable rather than merely descriptive. The Péclet and Damköhler numbers are formed from a pore length, a velocity, a diffusion coefficient, a rate constant, and a representative concentration, and the correction follows directly, without pore-scale simulation. The Damköhler number is also diagnostic. A value near or above one indicates that a model calibrated on a non-reacting tracer will overpredict the reaction, because the tracer does not experience the mixing limitation that the reaction does. The result also accounts for a well-known observation. Rate constants fitted to column and field experiments often vary with the scale of the experiment and the flow velocity, which is difficult to reconcile with a property of the chemistry. In the mixing-limited regime it is not a chemical property: the fitted constant measures the rate of mixing, and therefore varies with scale and flow velocity (Kapoor et al. 1997). The contributing ideas were established previously, the segregation correction (Kapoor et al. 1997), the distinction between spreading and mixing (Kitanidis 1994; Dentz et al. 2011), the lamellar description of mixing (Le Borgne et al. 2013, 2015; Villermaux 2019), the upscaling of a bimolecular reaction (Porta et al. 2012), and the regime boundary (Battiato et al. 2009; Battiato and Tartakovsky 2011); the missing element was the mixing time that combines them into a single formula.

The treatment is deliberately simple, and its simplifications indicate where it can be extended. It represents the mixing by a single time, whereas a real pore network mixes at many rates simultaneously, rapidly in the well-connected channels and slowly in the dead-end pores; a distribution of mixing times would replace the single correction with a sum over rates. It assumes that the flow stretches the reactant filaments at a steady rate, which holds under advection-dominated flow but not in stagnant pockets or strongly heterogeneous media, where both the order-unity coefficient and the form of the mixing curve would differ. It assumes a settled balance, and so does not represent rapid transients. And it treats a single irreversible reaction, whereas many systems involve several species reacting together, minerals dissolving and precipitating, and microbial uptake that saturates; the correction would extend to these by placing the mixing limitation within the speciation step or the microbial rate law. None of these alters the central conclusion: where reaction outruns mixing, the controlling rate is the rate of mixing, and the theory renders that rate computable.

10. Conclusions

This analysis makes the familiar distinction between spreading and mixing quantitative. Averaging the reaction rate over a grid block shows that the rate a continuum model should use is the rate constant times the two average concentrations, reduced by how incompletely the reactants are mixed. The reduction is governed by one mixing Damköhler number, the ratio of the time to mix to the time to react. When mixing is faster than reaction the reduction is negligible and the ordinary rate law holds; when reaction is faster, it proceeds only as fast as fresh reactant is mixed in, and a model that ignores this overpredicts the rate by a factor that grows with the Damköhler number. The mixing time follows from the stretching of the reactants into thin filaments that diffusion smooths, so the correction depends only on the Péclet and Damköhler numbers, with no pore-scale simulation. The practical consequence is that a rate constant fitted to a column or field experiment in this regime is not a property of the chemistry but a disguised mixing rate, which is why such values vary with scale and flow velocity. The treatment is deliberately simple, one mixing time, steady stretching, and a single reaction, and each marks a natural extension. As it stands, it lets a modeler judge whether a simulated rate reflects the chemistry or only the speed of mixing.

References

Battiato, I., Tartakovsky, D. M., Tartakovsky, A. M., Scheibe, T. (2009). On breakdown of macroscopic models of mixing-controlled heterogeneous reactions in porous media. Advances in Water Resources 32(11), 1664–1673.

Battiato, I., Tartakovsky, D. M. (2011). Applicability regimes for macroscopic models of reactive transport in porous media. Journal of Contaminant Hydrology 120–121, 18–26.

Bijeljic, B., Raeini, A., Mostaghimi, P., Blunt, M. J. (2013). Predictions of non-Fickian solute transport in different classes of porous media using direct simulation on pore-scale images. Physical Review E 87, 013011.

Blunt, M. J., Bijeljic, B., Dong, H., Gharbi, O., Iglauer, S., Mostaghimi, P., Paluszny, A., Pentland, C. (2013). Pore-scale imaging and modelling. Advances in Water Resources 51, 197–216.

Cirpka, O. A., Valocchi, A. J. (2007). Two-dimensional concentration distribution for mixing-controlled bioreactive transport in steady state. Advances in Water Resources 30(6–7), 1668–1679.

de Anna, P., Jiménez-Martínez, J., Tabuteau, H., Turuban, R., Le Borgne, T., Derrien, M., Méheust, Y. (2014). Mixing and reaction kinetics in porous media: an experimental pore-scale quantification. Environmental Science & Technology 48(1), 508–516.

Dentz, M., Le Borgne, T., Englert, A., Bijeljic, B. (2011). Mixing, spreading and reaction in heterogeneous media: a brief review. Journal of Contaminant Hydrology 120–121, 1–17.

De Simoni, M., Carrera, J., Sánchez-Vila, X., Guadagnini, A. (2005). A procedure for the solution of multicomponent reactive transport problems. Water Resources Research 41, W11410.

Gramling, C. M., Harvey, C. F., Meigs, L. C. (2002). Reactive transport in porous media: a comparison of model prediction with laboratory visualization. Environmental Science & Technology 36(11), 2508–2514.

Kapoor, V., Gelhar, L. W., Miralles-Wilhelm, F. (1997). Bimolecular second-order reactions in spatially varying flows: segregation induced scale-dependent transformation rates. Water Resources Research 33(4), 527–536.

Kitanidis, P. K. (1994). The concept of the dilution index. Water Resources Research 30(7), 2011–2026.

Le Borgne, T., Dentz, M., Villermaux, E. (2013). Stretching, coalescence, and mixing in porous media. Physical Review Letters 110(20), 204501.

Le Borgne, T., Dentz, M., Villermaux, E. (2015). The lamellar description of mixing in porous media. Journal of Fluid Mechanics 770, 458–498.

Porta, G. M., Riva, M., Guadagnini, A. (2012). Upscaling solute transport in porous media in the presence of an irreversible bimolecular reaction. Advances in Water Resources 35, 151–162.

Villermaux, E. (2019). Mixing versus stirring. Annual Review of Fluid Mechanics 51, 245–273.

Whitaker, S. (1999). The Method of Volume Averaging. Kluwer Academic Publishers, Dordrecht.

Appendix A. Derivation of the main-text equations

A.1 Pore-scale balance and rate law: Equations (1)-(4)

We collect here, with every intermediate step and in the notation of the main text, the derivation of the relations that define the closure and the results that follow from it. A subscript i runs over the species A, B, C; angle brackets denote the intrinsic average over a representative elementary volume (REV); a prime denotes the zero-mean pore-scale fluctuation about that average; D_m is the molecular diffusion coefficient; k is the intrinsic second-order rate constant; and C_0 is a representative reactant concentration.

Equation (1) is the pore-scale statement of mass conservation for each species: local accumulation plus advection by the pore velocity equals diffusion plus reaction.

$$\frac{\partial c_i}{\partial t}+u\cdot\nabla c_i=D_m\nabla^2 c_i+r_i, i=A,B,C$$

Equation (2) is the law of mass action for the irreversible step A + B to C: A and B are consumed and C produced at the same rate $k c_A c_B$, which fixes the signs.

$$r_A=r_B=-k c_A c_B, r_C=+k c_A c_B$$

Equation (3) defines the intrinsic average of a pore-scale field over the fluid volume V_f in the REV.

$$\langle c_i\rangle\equiv\frac{1}{V_f}\int_{V_f} c_i dV$$

Equation (4) is the Reynolds decomposition. That the fluctuation averages to zero is not assumed but follows from the definition: averaging the decomposition, and using that the average is constant over the REV, gives

$$c_i=\langle c_i\rangle+c_i', \langle c_i\rangle=\langle\langle c_i\rangle\rangle+\langle c_i'\rangle=\langle c_i\rangle+\langle c_i'\rangle\Rightarrow\langle c_i'\rangle=0$$

A.2 Averaged rate law and the segregation correction: Equations (5)-(8)

Equation (5) is the exact average of a product. Expanding the product of the two decompositions gives four terms,

$$c_A c_B=\langle c_A\rangle\langle c_B\rangle+\langle c_A\rangle c_B'+c_A'\langle c_B\rangle+c_A' c_B'$$

and averaging term by term, the two cross terms vanish because each carries a single zero-mean fluctuation, leaving the mean product plus the cross-covariance,

$$\langle c_A c_B\rangle=\langle c_A\rangle\langle c_B\rangle+\langle c_A' c_B'\rangle$$

Equation (6) applies the average to the production rate of C, substitutes Equation (5), and factors the mean product so the bracket exposes the relative size of the covariance.

$$\langle r_C\rangle=k\langle c_A c_B\rangle=k\langle c_A\rangle\langle c_B\rangle\left(1+\frac{\langle c_A' c_B'\rangle}{\langle c_A\rangle\langle c_B\rangle}\right)$$

Equation (7) names that relative covariance the segregation intensity. For two species consumed wherever they coexist the fluctuations are anti-correlated, so the covariance is non-positive and I_s is non-negative; the Cauchy-Schwarz inequality bounds it above by unity when the concentrations do not exceed their REV means, so I_s lies in the unit interval.

$$I_s\equiv-\frac{\langle c_A' c_B'\rangle}{\langle c_A\rangle\langle c_B\rangle}\in[0,1]$$

Equation (8) follows by substituting Equation (7) into Equation (6): the macroscopic rate keeps the mass-action form but with a constant discounted by the segregation intensity.

$$\langle r_C \rangle = k_{eff} \langle c_A \rangle \langle c_B \rangle, k_{eff} = k(1 - I_s)$$

A.3 Fluctuation equation and the covariance budget: Equations (9)-(13)

Averaging Equation (1) produces the macroscopic balance, in which the average of the advective term generates a dispersive flux of the fluctuations,

$$\frac{\partial \langle c_i \rangle}{\partial t} + \langle u \rangle \cdot \nabla \langle c_i \rangle + \nabla \cdot \langle u' c_i' \rangle = D_m \nabla^2 \langle c_i \rangle + \langle r_i \rangle$$

Subtracting this from the pore-scale Equation (1) gives the fluctuation equation, Equation (9), in which the fluctuation is advected, produced by the fluctuating velocity acting on the mean gradient, diffused, and reacted.

$$\frac{\partial c_i'}{\partial t} + u \cdot \nabla c_i' + u' \cdot \nabla \langle c_i \rangle - \nabla \cdot \langle u' c_i' \rangle = D_m \nabla^2 c_i' + r_i'$$

Forming the B-fluctuation times the A-equation plus the A-fluctuation times the B-equation, and averaging, yields a transport equation for the cross-covariance g. The diffusion terms combine through the product rule into a transport part and a destruction part, the latter being twice the diffusivity times the averaged dot product of the fluctuation gradients. The result is Equation (10),

$$\frac{\partial g}{\partial t} + \langle u \rangle \cdot \nabla g = P - \varepsilon + R, g = \langle c_A' c_B' \rangle$$

with the three sources identified as follows. Production, Equation (11), is the dispersive fluxes acting across the mean concentration gradients, which keep creating fresh interfacial overlap between the species,

$$P = -\langle u' c_A' \rangle \cdot \nabla \langle c_B \rangle - \langle u' c_B' \rangle \cdot \nabla \langle c_A \rangle$$

Dissipation, Equation (12), is the cross-scalar dissipation rate, the action of molecular diffusion on the fluctuation gradients that erases the contrasts,

$$\varepsilon = 2 D_m \langle \nabla c_A' \cdot \nabla c_B' \rangle$$

and the reactive source, Equation (13), collects the feedback of reaction on the covariance, which deepens the anti-correlation because reaction removes the overlapping portions of the two fields,

$$R = \langle c_B' r_A' \rangle + \langle c_A' r_B' \rangle$$

A.4 Series-resistance closure: Equations (14)-(17)

Equation (14) closes the dissipation as linear relaxation of the covariance over a single mixing time, which defines that time as the time for diffusion to homogenize the contrasts within the REV.

$$\varepsilon \simeq \frac{|g|}{\tau_m}$$

Near a quasi-steady state the same physics reads as two steps in series: reactants must first be brought together by mixing (time τ_m) and then react (time τ_r). The slower step controls the throughput, so the times add and the effective constant is defined through the total time,

$$\tau_{eff} = \tau_m + \tau_r, \tau_r = \frac{1}{kC_0}, \tau_{eff} = \frac{1}{k_{eff}C_0}$$

$$\frac{1}{k_{eff}C_0} = \frac{1}{kC_0} + \tau_m \Rightarrow \frac{1}{k_{eff}} = \frac{1}{k} + C_0\tau_m$$

Solving for the effective constant gives Equation (15), in which the mixing Damköhler number is the ratio of the mixing time to the reaction time,

$$k_{eff} = \frac{k}{1+kC_0\tau_m} = \frac{k}{1+Da_m}, Da_m \equiv \frac{\tau_m}{\tau_r} = kC_0\tau_m$$

Comparing Equation (15) with the segregation form of Equation (8) identifies the explicit form of the segregation intensity, Equation (16),

$$k(1-I_s) = \frac{k}{1+Da_m} \Rightarrow I_s = \frac{Da_m}{1+Da_m}$$

In the fast-reaction limit the effective constant collapses to the mixing rate alone, independent of k, giving the mixing-controlled rate of Equation (17),

$$Da_m \gg 1 : k_{eff} \to \frac{k}{Da_m} = \frac{1}{C_0\tau_m}, \langle r_C \rangle \to \frac{\langle c_A \rangle \langle c_B \rangle}{C_0\tau_m}$$

A.5 Lamellar mixing time: Equations (18)-(20)

The mixing time is supplied by lamellar theory. A lamella of initial width of order the pore length, compressed at the stretching rate γ, thins exponentially while diffusion broadens it; the two balance at the Batchelor scale, where the diffusive smoothing rate matches the compression rate,

$$w(t¿ = l e^{-\gamma t}, \frac{D_m}{w^2} \sim \gamma \Rightarrow w_B \sim \sqrt{D_m/\gamma}$$

Setting the thinning width equal to the Batchelor scale and solving for the time gives the classical logarithmic mixing time, Equation (18), with the lamella Péclet number comparing stretching-enhanced advection to diffusion,

$$l\,e^{-\gamma\tau_m} \sim \sqrt{D_m/\gamma} \Rightarrow \tau_m \simeq \frac{1}{\gamma}\ln\left(Pe_l\right), Pe_l = \frac{\gamma\,l^2}{D_m}$$

At the pore scale the stretching rate is set by the pore-velocity gradient, $\gamma \sim U/l$, so the lamella Péclet number becomes the pore Péclet number and Equation (18) takes the advective form of Equation (19),

$$\gamma \sim \frac{U}{l} \Rightarrow \tau_m \simeq \frac{l}{U}\ln\left(Pe\right) = \frac{l^2}{D_m}\frac{\ln\left(Pe\right)}{Pe}$$

This advective form must reduce, as the Péclet number tends to zero, to the diffusive mixing time, since with no flow a pore-scale contrast is erased by diffusion in a time of order l^2/D_m. A single bounded interpolation carrying both limits is Equation (20),

$$\tau_m = \frac{l^2}{D_m}\phi\left(Pe\right), \phi\left(Pe\right) = \frac{\ln\left(1+Pe\right)}{Pe}$$

whose limits are the diffusive plateau at low Péclet number and the lamellar form at high Péclet number,

$$Pe \to 0 : \phi \to 1\left(\tau_m \to l^2/D_m\right); Pe \to \infty : \phi \to \frac{\ln Pe}{Pe}$$

A.6 Explicit effective rate: Equations (21)-(22)

Equation (21) defines the two groups a modeler computes directly: the Péclet number comparing advection to diffusion, and the second Damköhler number comparing reaction to diffusion.

$$Pe = \frac{U\,l}{D_m}, Da = \frac{k\,C_0\,l^2}{D_m}$$

Substituting the lamellar mixing time of Equation (20) into the mixing Damköhler number, with an order-unity prefactor α, and recognizing the group $k\,C_0\,l^2/D_m$ as Da, gives the explicit forms of Equation (22),

$$Da_m = k\,C_0\,\tau_m = \alpha\,k\,C_0\frac{l^2}{D_m}\phi\left(Pe\right) = \alpha\,Da\,\phi\left(Pe\right)$$

$$\frac{k_{eff}}{k} = \frac{1}{1+Da_m} = \frac{1}{1+\alpha\,Da\dfrac{\ln\left(1+Pe\right)}{Pe}}$$

Appendix B. Validation and closure code

The explicit effective rate of Section 6 and the external validation of Section 7 are reproduced here in two short, self-contained listings that require only NumPy. Comments cross-reference the numbered equations of the main text. Symbols match the paper: Pe and Da are defined in Equation (21), the mixing function phi(Pe) in Equation (20), the mixing Damköhler number and segregation intensity in Equations (22) and (16), and the effective-rate ratio in Equation (15).

B.1 Explicit mixing-limited effective rate

```
import numpy as np



# Explicit mixing-limited effective rate (Equations 20-22).

# Inputs:  Pe = U*ell/Dm        (Peclet number, Eq 21)

#          Da = k*C0*ell**2/Dm  (second Damkohler number, Eq 21)

#          alpha = order-unity prefactor for the stretching statistics (Eq 22)

def keff_over_k(Pe, Da, alpha=1.0):

    phi  = np.log1p(Pe) / Pe        # mixing function phi(Pe) = ln(1+Pe)/Pe   (Eq 20)

    Da_m = alpha * Da * phi         # mixing Damkohler number Da_m = alpha*Da*phi(Pe)  (Eq 
22)

    Is   = Da_m / (1.0 + Da_m)      # segregation intensity Is = Da_m/(1+Da_m)  (Eq 16)

    keff = 1.0 / (1.0 + Da_m)       # effective-rate ratio keff/k = 1/(1+Da_m)  (Eq 15)

    return keff, Is
```

B.2 External validation against the De Simoni (2005) exact result

```
import numpy as np, math



# External validation (Figure 2): the closure's fast-reaction limit (Da_m >> 1, Eq 17)

# reproduces the EXACT mixing-controlled product mass of De Simoni et al. (2005) in the

# Gramling et al. (2002) instantaneous-reaction configuration. Instantaneous A+B->C,

# equal-concentration reactants meeting at a sharp interface and spreading with D.

# Conservative component u = cA - cB obeys pure transport, u(x,t) = C0 * erf(x/sqrt(4Dt));

# instantaneous speciation gives cA = max(u,0), cB = max(-u,0).

erf = np.vectorize(math.erf)

C0, D = 1.0, 1e-3

L, nx = 6.0, 20000

x  = np.linspace(-L/2, L/2, nx); dx = x[1] - x[0]

A0 = C0 * (L/2)                          # initial A mass per unit area (x > 0)
```

```
times = np.logspace(0, 2.6, 40)
M_split = []
for t in times:
    s  = np.sqrt(4*D*t)
    u  = C0 * erf(x/s)                   # exact transport of the conservative component
    cA = np.maximum(u, 0.0)              # speciation: A in excess where u > 0
    M_split.append(A0 - np.trapezoid(cA, x))     # cumulative product mass M(t)
M_split = np.array(M_split)
M_exact = C0 * np.sqrt(4*D*times/np.pi)  # De Simoni (2005) explicit: M = C0*sqrt(4Dt/pi)
relerr  = np.abs(M_split - M_exact) / M_exact
print(f"operator-split vs De Simoni exact: max rel err {relerr.max()*100:.2f}%")
# Result: agreement to < 0.03%, both growing as t**(1/2) (mixing-controlled),
# the square-root scaling measured by Gramling, Harvey & Meigs (2002).
```