



Enhanced reaction kinetics and reactive mixing scale dynamics in mixing fronts under shear flow for arbitrary Damköhler numbers

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ABSTRACT

Mixing fronts, where fluids of different chemical compositions mix with each other, are known to represent hotspots of chemical reaction in hydrological systems. These fronts are typically subjected to velocity gradients, ranging from the pore scale due to no slip boundary conditions at fluid solid interfaces, to the catchment scale due to permeability variations and complex geometry of the Darcy velocity streamlines. A common trait of these processes is that the mixing interface is strained by shear. Depending on the Péclet number Pe , which represents the ratio of the characteristic diffusion time to the characteristic shear time, and the Damköhler number Da , which represents the ratio of the characteristic diffusion time to the characteristic reaction time, the local reaction rates can be strongly impacted by the dynamics of the mixing interface. So far, this impact has been characterized mostly either in kinetics-limited or in mixing-limited conditions, that is, for either low or high Da . Here the coupling of shear flow and chemical reactivity is investigated for arbitrary Damköhler numbers, for a bimolecular reaction and an initial interface with separated reactants. Approximate analytical expressions for the global production rate and reactive mixing scale are derived based on a reactive lamella approach that allows for a general coupling between stretching enhanced mixing and chemical reactions. While for $Pe < Da$, reaction kinetics and stretching effects are decoupled, a scenario which we name "weak stretching", for $Pe > Da$, we uncover a "strong stretching" scenario where new scaling laws emerge from the interplay between reaction kinetics, diffusion, and stretching. The analytical results are validated against numerical simulations. These findings shed light on the effect of flow heterogeneity on the enhancement of chemical reaction and the creation of spatially localized hotspots of reactivity for a broad range of systems ranging from kinetic limited to mixing limited situations.

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1. Introduction

Reaction fronts where two reactive fluids displace one another play an important role in a range of processes, including contaminant plume transport and reaction, soil and aquifer remediation, CO_2 sequestration and the development of hotspots of reaction in mixing zones (Dentz et al., 2011; Fu et al., 2015b; Hidalgo et al., 2015; Ovchinnikov and Zeldovich, 1978; Saaltink et al., 2013; Tartakovsky et al., 2009; Tel et al., 2005). Mixing of reactants by heterogeneous flows leads to the formation of geometrically-complex fronts, at which chemical reactions occur (Chiogna et al., 2012; Cirpka et al., 2011; Cirpka and Valocchi, 2007; De Simoni

et al., 2007; Dentz and de Barros, 2015; Fu et al., 2015a; Hochstetler and Kitanidis, 2013; Rajaram and Gelhar, 1993; Sanchez-Vila et al., 2007; Werth et al., 2006; Willmann et al., 2010). Such fronts are subjected to fluid deformation which increases the surface available for diffusive mass transfer thereby enhancing effective reaction rates (de Anna et al., 2014b; De Wit, 2001; Finn and Thiffeault, 2011; Le Borgne et al., 2014; Ottino et al., 1979; Ou and Ranz, 1983; Weiss and Provenzale, 2008).

The dynamics of reactive mixing systems has been widely studied in the absence of velocity gradients. Galfi and Racz (1988) and Larralde et al. (1992) studied diffusion coupled to the reversible bimolecular reaction $A + B \rightleftharpoons C$ for the case of initially well separated reactants at different bulk concentrations. The mathematical insights obtained through the long-time asymptotics are that the mass of product formed, m_c , grows as $m_c \sim t^{1/2}$, which is expected from the diffusive flux across the interface, while the width of the reaction front s_r grows as $s_r \sim t^{1/6}$, due to the balance between the

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diffusive growth and the reactive consumption. Taitelbaum et al. (1991) have studied the initial time dynamics of such reactive fronts for a bimolecular reaction and showed that the rate of production of the product grows as $t^{1/2}$ as opposed to the asymptotic long-time limit t^{-1} . For a similar reactive front, Arshadi and Rajaram (2015) found by means of regular perturbation analysis that the growth rate of the total product mass behaves as $dm_c/dt \sim t^{1/2}$ at short times while at larger times it evolves as $dm_c/dt \sim t^{-1/2}$; the transition time between the two regimes is shown to depend on the rate constant and diffusion coefficient. Similar observations of the kinetic diffusive regimes were observed in the work by Chopard et al. (1993) who focused on quantification of the influence of the reversible reaction in comparison to the forward reaction, with an emphasis on the formalism of cellular automata. This problem was also addressed through a mean-field formalism for species with different reactivities by Sinder and Pelleg (2000) with the product formed being immobile. Results for reactive fronts for the annihilation reaction ($A + B \rightarrow \Phi$) were obtained through probabilistic cellular automata for a 1D case (Cornell, 1995) where it was shown that the reaction width grows as $w \sim t^{1/4}$. The validity of the analytical results were then investigated for higher dimensions by Howard and Cardy (1995). They found that the characteristic time of the crossover between the initial time irreversible and the long time reversible behavior depends on the inverse of the Damköhler number written in terms of the reversible kinetics rate constant. Several other works relate to reaction-diffusion waves in autocatalytic systems ($A + nB \rightarrow (n+1)B$) Merkin and Needham (1989) where the front propagation velocity is obtained analytically in the long time limit. Merkin et al. (1989), Merkin and Needham (1990), Gray et al. (1990) also developed solutions for the situations of well stirred mixtures and low catalyst concentrations where the catalyzer decays in time through a parallel reaction ($B \rightarrow C$). Taitelbaum (1993) studied the influence of initial conditions and fluctuations on the segregation and patterns formed by such bimolecular systems. Taitelbaum et al. (1996) studied the influence of bias on the reaction kinetics of bimolecular reactive fronts. This study was motivated by the observations of Koo and Kopelman (1991) that the reaction kinetics of injected fronts, i.e. without a stationary front, do not follow the analytical predictions of Galfi and Racz (1988). Park et al. (2001) performed experiments to prevent the advective motion of such injections and showed that the analytical predictions of the scalings of the reactive fronts agrees well with experimental observations of copper ion-complex formation reactions. Havlin et al. (1995) and Bazant and Stone (2000) have also considered the scenario of diffusion-reaction kinetics for a system with one static component (for example, a solid porous catalyst). Through analytical solutions, Taitelbaum and Koza (1998) have shown that the reaction fronts for initially well separated reactants may move forward or backward depending upon the relative diffusivity of the two species reacting species (see also Koza, 1996; Polanowski and Koza, 2006). Benson et al. (2013) have analyzed an annihilation reaction between two reactants to study the mixing density. Sinder et al. (2011) analyzed the reactive boundary layer between a two species reversible reaction system ($A \leftrightarrow B$) by means of a singular perturbation analysis for fast reactions, i.e. where the characteristic reaction time is much smaller than the characteristic diffusion time. On similar lines, Sinder and Pelleg (2002) analyzed a system with two competing reactions and found analogous irreversible initial regimes followed by a crossover regime depending on the reaction kinetics. It is shown that the reversible time regime encompasses two distinct reversible and irreversible zones near the reaction front. When velocity gradients exist in a fluid flow, transported reactive mixtures are submitted to repeated stretching actions that lead to the formation of elongated lamellar structures. The latter are known to promote mixing and enhance reaction rates (Allègre and Turcotte, 1986; Meunier and Villiermaux, 2010; Neufeld and Hernández-García, 2009; Ottino, 1989; Ottino et al., 1979; Rhines and Young, 1983; Villiermaux and Rehab, 2000). This problem was studied by Ranz (1979), who showed that the coupling of lamella deformation with diffusion can be reduced to a 1D diffusion reaction-diffusion equation by making use of (i) the rescaled coordinate perpendicular to the direction of lamella elongation and (ii) the so-called warped time that rescales temporal increments with the lamella elongation to eliminate the stretching term. Qualitative insights about the coupling of stretching-enhanced mixing and chemical reactions were obtained in Ou and Ranz (1983), Clifford (1999), Clifford et al. (1998) based on numerical simulations. Le Borgne et al. (2014) investigated the impact of non-uniform flow conditions on the mixing and reaction rates under such conditions using a lamellar mixing front approach. Paster et al. (2015) investigated the impact of shear upon reaction for uniformly initial distribution of reactants with concentration fluctuations.

Fluid stretching has been shown to play a fundamental role for governing mixing in porous media (Battiato et al., 2009; 2011; Boso and Battiato, 2013; Hyman et al., 2012; Villiermaux, 2012). The presence of heterogeneity in the advective flow field invariably leads to lamella formation and subsequent coalescence (Bolster et al., 2016; Le Borgne et al., 2013; 2015; Rolle and Kitandis, 2014). Therefore, understanding the interaction between the invading fluid and the residing fluid is imperative towards prediction of species transport in such media. For example, Mays and Neupauer (2012) have demonstrated a methodology to achieve enhanced mixing inducing chaotic Darcy-like flow patterns. Gramling et al. (2002) performed an experimental and theoretical Darcy scale study of the reaction rate and moving front width in a porous medium for the irreversible bimolecular reaction $A + B \rightarrow C$. They provided hints that incomplete pore-scale mixing was limiting local reaction rates, based on the inability of a Darcy scale modeling approach to properly predict the longitudinal concentration profiles and total mass of product. Later, de Anna et al. (2014b) investigated the impact of pore-scale mixing on chemical reactions in a two-dimensional (2D) porous medium consisting of cylindrical grains allowing to measure the 2D concentration field at the pore scale. They confirmed the role of mixing in controlling local reaction rates and were able to quantitatively predict the temporal evolution of the measured product mass in the infinite Damköhler limit (i.e. for fast reactions) using an upscaling theory based on the concept of lamellar reaction front (Jiménez-Martínez et al., 2015). Oates (2007) and later Chiogna and Bellin (2013) used a concentration probability density function (PDF) based mixing model to quantify the observed reaction rates in the experimental setup of Gramling et al. (2002).

In this work, we focus on reactive mixing of the bimolecular reaction $A + B \rightarrow C$ under shear flow, which represents a fundamental fluid deformation and reaction process in porous media. Shear occurs for any situations where adjacent parallel streamlines have different velocities. At the pore scale, shear is created by strong velocity gradients near fluid-solid interfaces (de Anna et al., 2014b). At the Darcy scale, shear flow is the dominant fluid stretching mechanism governing mixing and spreading in randomly stratified media, typical of sedimentary formations, where the horizontal correlation length is much larger than the vertical one (Bolster et al., 2011; Dentz and Carrera, 2007; Fiori and Dagan, 2002; Matheron and De Marsily, 1980; Weeks and Sposito, 1998). More generally, shear plays an important role in heterogeneous porous media as one of the components of local deformation tensors (Barros et al., 2012; Le Borgne et al., 2015). While linear shear flows give rise to a linear elongation of mixing fronts, other stretching dynamics could be considered in the same framework, such as power law (Le Borgne et al., 2015) or exponential (Lester et al., 2016) deformation (which implies that the length of a

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