Analysis of Two-Species Reaction-Diffusion with Applications to Chemical Oxidation of DNAPLs in Fractured Rock

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Abstract. This study was motivated by a problem arising in the context of chemical oxidation of dissolved DNAPL in a rock matrix by delivering oxidants such as permanganate through fractures. Under continuous flushing/recirculation, the concentrations of permanganate are maintained at a constant level, while it diffuses into the rock matrix and reacts with the DNAPL. The permanganate-DNAPL reaction is typically described as a bimolecular reaction, based on experimental kinetic data. Due to the relatively rapid rate of the oxidation reaction, an appropriately defined Damkohler number is large. Under these conditions, a thin reaction front develops and propagates into the rock matrix at a rate controlled by diffusion. A mathematical analysis of the dynamics of this reaction front is presented. The reaction front can be described as a moving boundary by analogy with the classical Stefan problem in heat transfer with phase change. The propagation of the reaction front can be quantified using a reaction front diffusivity, which can be calculated explicitly. The reaction front diffusivity is shown to depend on the initial concentrations of DNAPL and oxidant, and their effective diffusivities. Scaling arguments are proposed to quantify the temporal dynamics of the DNAPL consumption rate and the width of the reaction zone. The results of the analysis for (i) reaction front propagation, (ii) oxidant and DNAPL consumption rate and (iii) reaction zone width, are all confirmed by numerical simulations. An early time regime was identified, wherein the reaction front has yet to form. The duration of this early-time regime and a perturbation analysis to quantify the consumption rate are also presented. The consumption rate behaves as sqrt(t)) in this early time regime, transitioning to the diffusion-controlled 1/sqrt(t) behavior after the reaction front forms. At late time in a finite width of rock matrix, boundary effects are incorporated via an approximate integral balance approach. Numerical simulations in heterogeneous porous media indicate that the front is stable with respect to perturbations arising from natural heterogeneity, consistent with the few available field observations.