

## High-Resolution Experimental Investigation of mass transfer enhancement by chemical oxidation from DNAPL entrapped in variable-aperture fractures

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Permanganate oxidation of DNAPL- contaminated fractured rock is an effective remediation technology. Permanganate ion reacts with dissolved DNAPL in a bi-molecular oxidation-reduction reaction. The consumption of dissolved DNAPL in this reaction results in increased concentration gradients away from the free-phase DNAPL, resulting in reaction-enhanced mass transfer, which accelerates contaminant removal. The specific objective of our research was to perform high-resolution non-intrusive experimental studies of permanganate oxidation in a  $15.24 \times 15.24$  cm, transparent, analog, variable-aperture fracture with complex initial TCE entrapped phase geometry. Our experimental system uses light-transmission techniques to accurately measure both fracture aperture and the evolution of individual entrapped DNAPL blobs during the remediation experiments at high resolution (pixel size :  $6.2 \times 10^{-3}$  cm). Three experiments were performed with different flow rates and permanganate inflow concentrations to observe DNAPL-permanganate interactions across a broader range of conditions. Prior to initiating each experiment, the aperture field within the fracture was measured. The oxidation experiment was initiated by TCE injection into the water saturated fracture till the TCE reached the outflow end, followed by water re-injection through the fracture. The flowing water mobilized some TCE. We continued injection of water till TCE mobilization ceased, leaving behind the residual TCE entrapped within the variable-aperture fracture. Subsequently, permanganate injection through the fracture resulted in propagation of a fingered reaction front into the fracture. We are developing image processing algorithms to analyze the evolution of DNAPL phase geometry over the duration of the experiment. The permanganate consumption rate varied significantly within the fracture due to the complex flow and DNAPL concentration fields. Precipitated  $MnO_2$  was clearly evident on the downstream side of DNAPL blobs near the inflow boundary indicating high reaction rates in these regions. This behavior is explained by the diversion of permanganate around entrapped DNAPL blobs and downstream advection of dissolved DNAPL. Our results indicate that the total rate of mass transfer from the DNAPL blobs is higher at early times, when not much  $MnO_2$  has formed and precipitated. With time,  $MnO_2$  precipitation in the fracture leads to changes the aperture field and flow field. Precipitated  $MnO_2$  around TCE blobs also decreases the DNAPL accessible surface area. By comparing the results of three experiments, we conclude that low permanganate concentrations and high flow rates lead to more efficient DNAPL remediation, resulting from the fact that under these conditions there would be slower  $MnO_2$  formation and less precipitation within the fracture. We also present results on the time-evolution of fracture-scale permanganate consumption and DNAPL removal rates. The experimental observations are being used to develop improved high-resolution numerical models of reactive transport in variable-aperture fractures. The overall goal is to relate the coupled processes of DNAPL removal, permanganate consumption,  $MnO_2$  formation and associated changes in aperture and interface area; to derive fracture-scale effective representations of these processes.