

Kinetics Reaction Pathways of Hydroxyl Radical Production from Oxygenation of Reduced Iron Minerals and Their Reactivity with Trichloroethene: Simulating Real Environmental Scenarios

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Although reactive oxygen species (ROS) are known to be produced during the oxygenation of various ferrous species at groundwater field sites [1, 2], their impact on pollutant destruction remains uncertain. In this study, relatively real environmental scenarios were simulated in both batch experiments and a kinetic model, to investigate the mechanisms underlying the production of •OH and its reactivity towards trichloroethene (TCE) and competing species in the presence of reduced iron minerals (RIM), oxygen, and sulfate reducing bacteria (SRB). RIM slurries were prepared by combining varying amounts of Fe(II) and sulfide (with Fe(II):S ratios from 1:1 to 50:1), or Fe(II) and sulfate with SRB added. TCE and different levels of oxygen were introduced to the slurries, and the concentrations of TCE, •OH, and Fe(II) species were monitored over time. The extent of TCE oxidation and •OH production was greater when RIM was prepared under more reducing conditions (with more added Fe(II)) and then amended with O₂, and these reactions were either limited by O₂ or Fe(II). Kinetic rate constants suggest that •OH production from free Fe(II) (i.e., aqueous and ion-exchangeable) dominates •OH production from solid Fe(II) (i.e., adsorbed and structural), and that TCE competes with Fe(II) and organic matter (OM) for •OH. Competition with OM was observed only in systems that involved SRB. The results of the experiments suggest that cells and/or exudates may provide electron equivalents to regenerate Fe(II) from oxidized RIM. This was taken into account in the model by directly inputting the measured amounts of free and solid phase Fe(II) from the experiments, rather than through kinetic reactions. This work provides new insights into mechanisms of TCE destruction through •OH production resulting from RIM oxygenation in real environmental scenarios.

References:

[1] Schaefer, C.E., Ho, P., Berns, E., Werth, C (2018). Mechanisms for Abiotic Dechlorination of Trichloroethene by Ferrous Minerals under Oxic and Anoxic Conditions in Natural Sediments. *Environ. Sci. Technol.*, 52(23), 13747-13755.

[2] Schaefer, C.E., Ho, P., Berns, E., Werth, C (2021). Abiotic dechlorination in the presence of ferrous minerals. *J. Contam. Hydrol.*, 241, 103839.