

Entropy and reactive solute transport in porous media

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Mixing processes significantly affect reactive solute transport in porous media. Contaminant degradation in environmental aquatic systems can be limited either by the availability of one or more reactants, brought into contact by physical mixing, or by the kinetics of the (bio)chemical transformations. Appropriate metrics are needed to accurately quantify the interplay between mixing and reactive processes. The exponential of the Shannon entropy of the concentration probability distribution has been proposed and applied to quantify the dilution of conservative solutes either in a given volume (dilution index) or in a given water flux (flux-related dilution index). We propose using entropy-based metrics of mixing to reactive transport in porous media. Adopting a flux-related framework, we show that the degree of uniformity of the solute mass flux distribution for a reactive species and its rate of change are informative measures of physical and (bio)chemical processes and their complex interaction (Figure 1).

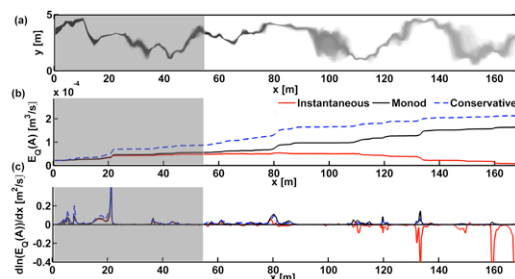


Figure 1: Steady-state conservative plume (a). Flux-related dilution index of compound A for the conservative and two reactive cases (b) and the spatial derivative of its natural logarithm (c) in a heterogeneous domain considering: instantaneous kinetics (red line), double Monod kinetics (black line) and conservative transport (blue dashed line).

Electrochemical investigation of iron monosulfide oxidation by hydrogen peroxide

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Aqueous oxidation of synthetic iron monosulfide (FeS) by H_2O_2 in HCl solutions was investigated by electrochemical techniques. Corrosion current densities (i_{corr}) and corrosion potentials (E_{corr}) were measured as a function of $[H_2O_2]$ (0.001 to 0.1 M) and pH (2 to 11) at temperatures from 30 to 45°C. Experiments were carried out in a conventional three electrode cell assembly with a Pt counter electrode and saturated calomel reference electrode.

It was found that, i_{corr} decreases (E_{corr} increases) from 0.27 mA cm⁻² (-364 mV) down to 0.019 mA cm⁻² (up to -57 mV) when pH increases from 2 to 5 (7). Thereafter they remain roughly constant up to pH 11. $[H_2O_2]$ and temperature have a more complex effect on FeS oxidative dissolution. At pH 2.5 and 45°C, i_{corr} increases from 0.16 mA cm⁻² ($[H_2O_2]=0.001$ M) up to 0.35 mA cm⁻² ($[H_2O_2]=0.002$ M), and then it decreases down to 0.2 mA cm⁻² ($[H_2O_2]=0.1$ M). In similar conditions, E_{corr} increases when $[H_2O_2]$ increases. At $[H_2O_2]=0.005$ M and pH 2.5, E_{corr} increases (i_{corr} decreases) from -348 mV (0.19 mA cm⁻²) up to -304 mV (down to 0.16 mA cm⁻²) when temperature increases from 30°C to 40°C (35°C). Thereafter E_{corr} decreases (i_{corr} increases) to -372 mV (0.24 mA cm⁻²).

The experimental results indicate that at low pH H_2O_2 is an effective oxidant of FeS. The complex effect of $[H_2O_2]$ and temperature on mineral aqueous oxidation is likely the result of the several reactions. Among these reactions we note: FeS oxidation; $[H_2O_2]$ decomposition and formed O_2 adsorption on mineral surface.

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