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Influence of 2D physical heterogeneity on the electromigration of nitrate

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Physical heterogeneity in the subsurface poses significant problems for the bioremediation of contaminants, these include: (1) delivery of biological amendments to stimulate bioremediation by hydraulic techniques is limited to soils and sediments with hydraulic conductivities above around 10^{-7} m s^{-1} [1]; and (2) physical heterogeneity imparts controls on the distribution and microscale mixing of microbes and solutes thus hindering biodegradation [2]. Electrokinetics (EK) is effective at initiating a number of different transport phenomena in materials with low hydraulic conductivities such as 10^{10} m s^{-1} [3]. The technique may therefore be suitable at delivering amendments under physically heterogeneous conditions[4].

The aim of this research is to determine the influence of 2D heterogeneity on the electromigration of nitrate. The objectives are: (1) to identify whether 2D heterogeneity imparts controls on the voltage gradient based on differences in the effective ionic mobility and subsequently the effective electrical conductivity; (2) whether these voltage gradient differences contribute to enhanced migration between sections of the 2D heterogeneous system; and (3) identify these phenomena in both idealised and natural sediments.

Electromigration theory indicates that changes in permeability can potentially have an effect on the mass flux. The description of 1D electromigration mass flux of ionic species, i is given [5]:

$$J_i = C_i(u_i^* - k_e) \frac{\partial E}{\partial x} \qquad (1)$$

Where J_i, electromigration mass flux (kg m^{-2} s^{-1}); C_i, solute concentration (kg m^{-3}); u_j^*, effective ionic mobility (m^2 V^{-1} s^{-1}); k_e, electroosmotic permeability (m^2 V^{-1} s^{-1}); E, electrical potential (V); x, distance (L). The ionic mobility is analogous with the diffusion coefficient:

$$u_i^* = u_i \, n \, \tau = \frac{D_i^* \, z_i \, F}{R \, T} \qquad (2)$$

Where u_i, ionic mobility (m^2 V^{-1} s^{-1}); n, porosity (-); τ, tortuosity (-); F, Faraday's constant (C mol^{-1}); z_i, valence of ion; D_i^*, effective diffusion coefficient (L^{2}T^{-1}); R, universal gas constant (J K^{-1} mol^{-1}); T, absolute temperature (K). The diffusion coefficient has been shown to decrease with permeability due to an increase in the tortuosity of the migration

path length [6]. Therefore if the ionic mobility varies spatially there will also be subsequent variations in the electromigration rate. Similarly, there will also be variation in the voltage gradient based on the relationship between the effective ionic mobility and the effective electrical conductivity [7]:

$$\frac{\partial E}{\partial x} = \frac{I - F\, \sum_{i=1}^{N} z_i D_i^* \frac{\partial C_i}{\partial x}}{\sigma^*} \qquad (3)$$

$$\sigma^* = \sum_{i=1}^{N} F\, z_i u_i^* C_i \qquad (4)$$

Where I, current density (C s^{-1} m^{-2}); σ*, effective electrical conductivity (S m^{-1}). Thus, in a physically heterogeneous setting where concentration of chemical species is uniform, the voltage gradient should increase in material with a low effective ionic mobility (i.e. low permeability material) relative to material with a high effective ionic mobility (i.e. high permeability material).

Experiments will be conducted in an experimental setup similar to Figure 1. There are three elements to the experimental design each with associated outcomes:

1. *Homogenous vs heterogeneous comparison*: homogeneous controls will be run using the same material type representing the low permeability section in the heterogeneous experiments. Differences in values for nitrate concentration and voltage gradient will be used to determine whether nitrate migration between layers is occurring.
2. *Varying nitrate inlet concentration between experiments*: this is to increase the proportion of the amendment in the total electrical conductivity of the electrolyte. It is expected that the high permeability section will have a higher associated effective ionic mobility, therefore, the higher the nitrate inlet concentration the greater the difference in electrical conductivity and voltage gradient between layers potentially leading to increased migration.
3. *Glass beads vs natural sediment*: selected homogenous and heterogeneous experiments will be repeated with natural sediment to observe whether this phenomena occurs in conditions more representative of the natural environment.
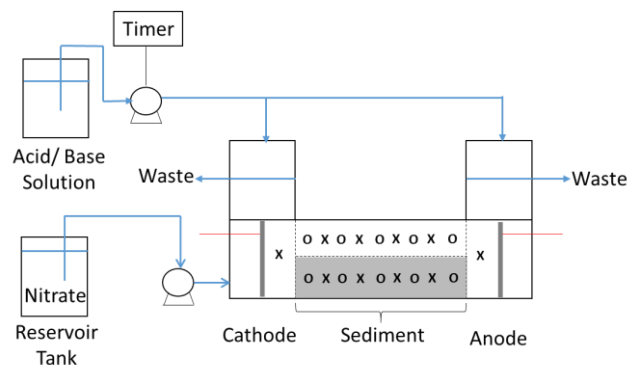

Figure 1. Reactor vessel schematic. Dark and light areas in the sediment chamber show the zones of low and high permeability X and O represent sampling and voltage probe ports.

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