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Effect of physical heterogeneity on the electromigration of nitrate in layered granular porous media

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ABSTRACT

The effect of physical heterogeneity on the electrokinetic (EK) transport of nitrate, an electron acceptor frequently used for anaerobic biodegradation, was investigated experimentally within saturated granular porous media comprising two layers of high and low hydraulic conductivity (K) material. Two hypotheses were tested: firstly, that the presence of layered physical heterogeneity will generate non-uniformities in the electric field; and secondly that this would create non-uniform electromigration of ions resulting in an additional nitrate flux into the lower-K layer. Experiments were conducted in bench-top test cells that contained electrode and sediment chambers. An aqueous nitrate solution (0, 0.1, 1 and 5 g-NO_3 L^{-1}) was added at the cathode and the experiments run with an idealised mixture of glass beads and kaolinite, and natural sediment and kaolinite. A constant current (1.6 A m^{-2}) was applied in all experiments. Results showed elevated voltage differences between layers in heterogeneous experiments compared to equivalent homogenous experiments. Furthermore, nitrate concentrations are elevated in the low-K material in heterogeneous compared with homogeneous systems. Using predicted values this is shown to be a function of a transverse flux associated with the voltage difference between layers. The importance of this phenomena at field scale for delivery of an amendment (i.e., electron acceptor, donor or nutrient) by EK for bioremediation is presented in an electron balance model. Overall, this research establishes and quantifies a previously unreported important phenomenon in the electrokinetic transport literature that enhance the application of this technology for bioremediation of contaminated aquifers.

1. Introduction

Aqueous phase contaminant plumes within physically heterogeneous aquifers (where hydraulic conductivity (K) varies) present a long-term management challenge. Contaminants can become sequestered in low-K zones within heterogeneous settings and persist as secondary sources of groundwater contamination. This occurs due to the presence of concentration gradients across the interface between a low-K zone and high-K host matrix that drives diffusion of contaminants into the low-K zone [1]. This concentration gradient is reversed after advection of contaminants from the high-K host matrix, resulting in back-diffusion of contaminants sequestered in the low-K zone into the host matrix over long timescales, which prolong remediation efforts [2] in situations where the mass flux relative to natural attenuation processes is sufficient to give rise to a site-specific risk. These scenarios are difficult to treat by conventional hydraulic-based techniques, such as pump and treat, due to this mass transfer limitation in low-K materials.

Electrokinetics (EK) is a technique that initiates solute transport phenomena independent of K, by applying direct current to porous media. EK processes comprise electromigration, electroosmosis and electrophoresis, which can be coupled with other technologies, such as bioremediation to enhance biodegradation of organic compounds *in situ*. At the micro-scale EK transport can increase mixing and improve contact between microorganisms, contaminants and nutrients to enhance bioaccessibility [3]; and at the macro-scale by increasing the supply of electron acceptors supporting biodegradation [4]. EK enhanced bioremediation (EK-BIO) is a potentially suitable technology to treat biodegradable compounds in physically heterogeneous settings, where EK can be used to overcome physical limitations on *in situ* biodegradation.

In advection-dominated systems there is limited flow across high- to low-K boundaries. Therefore, in physically heterogeneous settings bioremediation of low-K zones will be limited by the

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distribution and mixing of microbes and solutes [5]. In EK dominated systems physical heterogeneity is less inhibiting because the electric field is not directly affected by K. EK can be used to directly remove contaminants, such as lead and phenanthrene, from heterogeneous settings by electromigration and electroosmosis [6,7] and also introduce amendments within heterogeneous settings. For example, Reynolds et al. [8] migrated potassium permanganate into clay blocks within a high permeability host material to show the effectiveness of coupling EK with *in situ* chemical oxidation. However spatial changes in material type will still exert a control on solute migration by EK. Gill et al. [9] showed that the transition from high- to low-K porous media corresponds to a decrease in nitrate mass flux and increase in the voltage gradient. Both factors depend on the effective ionic mobility (EIM), itself a function of the porosity and tortuosity of a porous medium [10].

Electric fields in homogeneous 2-D settings can be non-uniform and create tortuous migration pathways for solute migration between electrodes [11]. Physical heterogeneity affects the arrangement of electric fields and will therefore create non-uniform flow paths relative to the distribution of high- and low-K zones [9]. These non-uniform flow paths are equivalent to fluxes and are important when trying to understand the efficacy of amendment delivery by EK in a remediation scenario.

The objectives of this study were to deduce the effect of EK transport on nitrate migration within homogeneous and heterogeneous settings, identify the controlling mechanisms for any differences observed and determine the influence of variations in nitrate concentration on amendment flux. Heterogeneity in this study is represented by two layers of granular porous media with different K values. The following hypotheses were tested:

1. A small voltage difference will exist between layers of material with different EIM values, due to the subsequent variation in ion mass flux into the sediment and effective electrical conductivity. Furthermore, this difference will increase with nitrate concentration;
2. This difference in voltage gradient will create an associated electromigration mass flux between layers and can be quantified by comparing nitrate transport in heterogeneous and homogeneous systems.

2. Materials and Methods

2.1. Material properties

The porous medium was created with two materials: soda-lime-silica glass beads (Potters Ballotini Ltd), to represent an ideal system, and silica sand (David Ball Group PLC and Marchington Stone Ltd), to represent natural sediment. Homogeneous and heterogeneous configurations of these materials were developed, the latter having a layered contrast between high- and low-K media. High-K and low-K material was produced for both glass beads and natural sediment (Table 1). High- and low-K material have respectively large and small grain sizes, with extra kaolin clay (Speswhite, Imerys Performance Materials Ltd) added to the low-K material to further reduce the K value. These are similar to the materials used in experimental work described in Gill et al. [9]. Further information on material properties and the consolidation method used for homogeneous experiments is in the supporting information (Sections S.1.1 and S.1.2 respectively). The layered K contrast was achieved by first wet packing the low-K material into the test cell until the compacted material filled half the chamber. The surface of the low-K material was smoothed with a metal spatula and the loose high-K material added above and consolidated using the shaker Table method (see supporting information, Section S.1.2). After the addition of high- and low-K material the chamber lid was secured before saturation of the media with synthetic groundwater.

A synthetic groundwater was used to simulate an electrical conductivity of 700 $\mu S\,cm^{-1}$, based on natural groundwater sampled in a UK aquifer [12]. This was achieved using a NaCl-deionised water solution (0.3 g-NaCl L^{-1}), prepared with deionised water sterilised by tangential flow filtration unit (1 μm filter). The test cells containing the consolidated material were saturated with synthetic groundwater from the base up at a low flow rate to remove entrapped air and then sealed.

2.2. Bench-scale setup

An experimental test cell was developed for the preparation of reproducible sections of packed materials with high- and low-K (Fig. 1). This is the same test cell used in Gill et al. [9], further details are in the supporting information, Section S.1.3.

After consolidation and enclosure of material in the test cell synthetic groundwater and the amendment solution was circulated at 10 mL min^{-1} from the reservoir tank into the cathode chamber using a peristaltic pump (Ismatec, REGLO MS-4/8). This was done until the fluid in the cathode chamber had been displaced to waste (approx. 3.5 h). A baseline sample of the pore fluid (using ports along the cell side) was taken before direct current was applied to the system from a power pack (Digimess, PM6003-3).

Samples of pore fluid for chemical analysis were taken every 2 days during the experiment, with the exception of a 4-day break between the 5th and 6th sampling time points (at days 10 and 14). Within the sediment chamber, eight narrow bore (ID = 0.5 mm) PEEK tubes were distributed in two rows of four, one for each of the high and low-K layers, with an extra sampling tube in each electrode chamber. Sampling tubes were placed inside the sediment chamber prior to consolidation and material packed around them. Blockages were prevented by fitting a small (5 × 10 × 20 mm) cube of porous sintered glass to the end of each tube. Each pore fluid sample was 1 mL to ensure minimal disturbance. Ten voltage probes consisting of 4 mm diameter 316 stainless steel rods housed in HDPE piping and distributed in two rows of five, one for each of the high and low-K layers. Voltage

Table 1
Properties of material used in experiments.

Material		Porosity, n (−)	K ($m\,s^{-1}$)	Grain Diameter (mm)	Relative composition (%)
Glass Beads	High-K	0.30	9.2×10^{-4} ($\pm 8.8 \times 10^{-5}$)	1.4	100
	Low-K	0.34	5.7×10^{-7} ($\pm 2.4 \times 10^{-7}$)	0.25	80
				0.50	10
				Kaolin	10
Silica Sand	High-K	0.39	7.0×10^{-4} ($\pm 4.9 \times 10^{-5}$)	2.4–1.2	100
	Low-K	0.44	5.9×10^{-7} ($\pm 2.8 \times 10^{-8}$)	<0.15	90
				Kaolin	10